POTENTIAL - pH RELATIONSHIPS OF SOME METAL-METAL OXIDE ELECTRODES

by

D.G. Jones B.Sc.

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TO ANNE AND MY PARENTS

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ABSTRACT

The suitability of metal-metal oxide electrodes and the drawbacks of established pH measuring electrodes are reviewed.

A well-established metal-metal oxide system was chosen for initial examination and various experimental techniques of evaluation were developed. This work was extended to include a brief investigation of certain other systems, bismuth, tungsten, platinum, rhodium and gold. Finally, the viability of an electrode prepared by the electrodeposition of rhodium was established and detailed studies made.

Further experiments were designed to determine the chemical and physical nature of the electrode surface, as well as the reactions responsible for some of the deviations from the theoretical pH response. The techniques employed for this purpose included Energy Dispersive Analysis, Stereoscan Electron Microscopy, X-ray Photoelectron Spectroscopy as well as various Electrochemical methods.

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Abbreviations

a	Constant
α	Bunsen Absorption Coefficient
b	Constant (Tafel slope: -2.3 RT/nF)
β	Ostwald Coefficient of Solubility
C	Number of Components (Phase Rule)
C	Capacity
C_{H^+}	Concentration of Hydrogen Ions Present in Solution
DPN	A Standard Measure of Metal Hardness
DVM	Digital Voltmeter
E	Electrode Potential
E^o	Standard Electrode Potential
E_e	Rest Potential (for electrochemical kinetic measurements)
E_g	Electrode Potential of Glass Electrode
E^o_g	Standard Electrode Potential of Glass Electrodes
E_s	Electromotive Force of a pH cell when introduced to a standard solution of known pH
E_x	Electromotive force of a pH cell when introduced to a solution of unknown pH
EDAX	Energy Dispersive Analysis
ESCA	Electron Spectroscopy for Chemical Analysis (see X.P.S.)
F	Faraday
F	Number of Degrees of Freedom (Phase Rule)
I	Current
I_o	Exchange Current
i	Current Density
i_o	Exchange Current Density
I.B.	Prefix for Established Universal Buffers

k	Gradient on Slope of Potential-pH line
k'	Constant (see Henry's Law)
m	Mass of Gas Dissolved in Unit Volume of Solvent
n	Number of Electrons Involved
η	Overpotential
Ox	Oxidized Species
P	Number of Phases (Phase Rule)
P_{O_2}	Partial Pressure of Oxygen
p	Pressure or partial pressure
pH	$-\log a_{H^+} \simeq -\log C_{H^+}$
pK	-log K (where K is the dissociation constant)
Q	Charge Transferred
R	Gas Constant
R	Resistance
Red	Reduced Species
T	Temperature in K
T_o	273K
t	time
TMAH	Tetramethylammonium hydroxide
U.B.	Prefix to Amine Universal Buffers
V	Volume of Solvent
v	Actual Volume of Gas Dissolved
v_o	Volume of Gas Dissolved at S.T.P.
X.P.S.	X-ray Photoelectron Spectroscopy

Chapter 1

GENERAL INTRODUCTION

The simple theoretical definition of pH as put forward by Sørensen is

$$pH = - \log C_{H^+} \qquad 1.1$$

where C_{H^+} is the concentration of hydrogen ions present in solution. The need for a precise definition of an experimental pH value and the fact that neither the concentration nor the activity of H^+ is measured by an electrometric method had led to pH being defined in an operational manner according to the following:

$$pH(X) = pH(S) + (E_x - E_s)/ k \qquad 1.2$$

In this equation, the terms E_x and E_s represent the electromotive force (e.m.f.) of a pH cell when introduced to a solution of unknown pH (pH(X)) and a standard solution of known pH (pH(S)) respectively. In this definition, the term k refers to a constant relating to a particular pH cell. This pH cell normally is assembled as follows:

Electrode reversible to hydrogen ions	unknown solution	bridge solution (3.5M KCl to saturated KCl)	reference electrode

The reference electrode referred to above usually takes the

form of a calomel (mercury-mercurous chloride) electrode or a silver-silver chloride electrode. When used in conjunction with a salt bridge these electrodes show an electrode potential which is independent of pH .

The other component electrode of the pH cell is called the indicator electrode or simply, the pH electrode. Ideally, this electrode should have a potential which varies with pH to the extent of -59.2 mV/pH at 25°C although the actual linear response of the electrode may fall below this value, provided it does so consistently and by a known amount. The value quoted above is obtained by applying the Nernst equation to the equilibrium for the hydrogen electrode:

$$H^+ + e^- \rightarrow \frac{1}{2} H_2 \text{ (g,1 atm)} \qquad 1.3$$

at 25°C. This yields the following expression:[2]

$$E = -\frac{2.3026\ RT}{F} pH \qquad 1.4$$

where E is electrode potential, R is the gas constant, T is the temperature in K and F is the faraday. It can be easily seen that this is the expression for a straight line where (-2.3026 RT/F) is the gradient i.e. -59.2 mV/pH at 25°C. If the conditions imposed in the last two paragraphs apply it is clear that the term k in equation 1.2 will have the value -59.2 mV/pH . This value is referred to as the "theoretical response". In this investigation k values are referred to as "pH responses", "gradients" and "slopes".

Since the hydrogen electrode provides the standard upon which

all other measurements are based, it has been widely used as an indicator electrode, particularly in cases where precision is of major importance. Essentially the electrode consists of a catalytic surface (normally a piece of platinum foil upon which finely divided platinum is deposited), over which a stream of hydrogen gas is slowly bubbled.

The hydrogen electrode not only offers the advantage of being accurate and reproducible but it has an unlimited range and a low resistance.[2] Unfortunately, it is also susceptible to a number of interferences.[2] Several substances are known to react irreversibly with the platinum-hydrogen system and hence adversely affect the performance of the electrode. Oxidizing agents such as the ferric ion, permanganates and chlorates have to be excluded as do chromates and nitrates under acidic conditions. In addition, hydrogen gas in contact with a catalytic surface such as finely divided platinum is a powerful reducing agent and consequently many reducible and inorganic materials have to be absent from solution.[2] This condition effectively excludes the platinum-hydrogen electrode for biological applications.

Another drawback of the hydrogen electrode is the tendency of the platinum surface to become "poisoned" by substances such as cyanides, lead, cadmium and thallous salts and by the cations of metals of "lower electromotive activity" than hydrogen.[2]

Although a number of the problems listed above can be solved, to a certain extent, by the use of thin 'platinum black' films or the substitution of palladium for platinum, a number of disadvantages are inherent: air has to be excluded from the solution under test and the hydrogen must be at near atmospheric pressure. Also

equilibration can take up to 60 minutes.[2] In addition, the equipment used for the hydrogen electrode is somewhat cumbersome and consequently this is not a convenient technique to use.

In view of the difficulties associated with the use of the hydrogen electrodes a number of secondary electrodes have been produced as alternatives but as yet, none have been produced with a range comparable to the hydrogen electrode or without other disadvantages. One such secondary electrode is known as the quinhydrone electrode.

This is essentially an oxidation-reduction electrode which is simply constructed by saturating the solution in the electrode compartment with quinhydrone and then immersing a bright gold or platinum electrode in it. The equilibrium involved can be written[2] as follows:

$$OC_6H_4O + 2H^+ + 2e = HOC_6H_4OH \qquad 1.5$$

This electrode gives a theoretical response from pH 0 to pH 8 . Unfortunately above this pH value an error becomes apparent. Furthermore this electrode is subject to a "salt error" in solutions containing high concentrations of electrolytes.

Like the hydrogen electrode, this electrode has a low resistance. The equilibrium time, in this case, is much lower and may be less than five minutes. One major advantage of this system over the hydrogen electrode is the comparative lack of interferents which makes this electrode more suitable for biological applications. Proteins and some amines, however, can cause appreciable errors.

The most widely used secondary pH indicator electrode, both

on an industrial and laboratory scale, is the glass electrode. The glass electrode, which belongs to the class of membrane electrodes, is highly specific for hydrogen ions over a very wide range of pH values.[2] Very simply this electrode consists of a thin glass bulb within which is mounted a reference electrode immersed in a solution of constant pH containing the ion to which the reference electrode is reversible.[3]

This electrode, which gives a theoretical pH response under most conditions, is extremely versatile, convenient to use and has a response time of less than one minute.[2] It is not susceptible to most of the interferents mentioned above in connection with the hydrogen and quinhydrone electrodes but unfortunately is subject to a number of disadvantages of its own.

One of the main disadvantages of this system in an industrial context is the inherent fragility of the materials involved. Unlike the electrodes mentioned previously the glass electrode has a very high electrical resistance (5 to 500 Megohms)[2] and varies with temperature. The need for specialized equipment to cope with these high resistances adds to the cost of construction.

All new glass electrodes have to be soaked in water or dilute buffer solution prior to use in order to acquire a pH response. If dehydration takes place, the variable asymmetry potential of the membrane may be altered resulting in the necessity for standardization. One of the major problems encountered in the use of glass electrodes is the "alkaline error", due to the presence of small cations, and observed at pH values above 11 . These effects can be minimized, however, by the use of special glasses or by applying corrections. Other disadvantages are the interferent effects of dehydrating

solutions, some colloids, fluorides and surface deposits on the electrode.

In view of the various drawbacks associated with the existing indicator electrodes, it is not surprising that there is a demand for a workable alternative. Ideally such an alternative should have a theoretical response over an unlimited range, a low response time and should be reproducible. It is also desirable that an indicator electrode of this sort should be convenient to use and not suffer from the interferences described above.

One system worth considering in this context is the metal-metal oxide electrode. Electrodes of this kind offer a number of advantages. They are inexpensive to construct and convenient to use. The inherent ruggedness of these systems offers obvious advantages, while the low electrical resistance eliminates one possible cause of sluggish responses and may remove the need for expensive electronic voltmeters that are essential for glass electrode work. These instruments may still be necessary, however, if the electrode is not completely reversible and prone to polarization. (See Antimony - Chapter 4.) It would be naive, of course, to expect a metal-metal oxide electrode to have a perfect response and also to be completely free from interferent effects. However, it is possible that an electrode could be produced which might prove useful under conditions abhorrent to established pH electrodes e.g. in industrial liquors which frequently prove detrimental to glass electrodes.

A metal-metal oxide electrode would probably be used to solve particular analysis problems over a small pH range, perhaps in highly alkaline solutions and under flow conditions. There is also

a demand for an electrode which may be used 'in vivo'. Such an electrode would be required to cover the pH range 6 to 8 .

It is more likely, however, that the electrode would be used under industrial conditions. For this reason, carbon dioxide and oxygen were not excluded during the early experimental work. The antimony-antimonous oxide system was chosen to begin the investigation partly in order to gain experience of these systems. It has been well researched in the past (see Chapter 4) and has already been investigated for Electronic Instruments Ltd. by Short (1963).[4]

The present work was instigated by E.I.L. in order to investigate reports of 'plateaux' in the potential-pH response curve of the antimony and other similar electrodes with a view to the possible production of a reference electrode over a limited pH range. It was quickly found by the examination of the literature available and from experimental work, that under 'aerated' conditions, the response was close to linear and that any deviations were due to the experimental techniques and solutions employed (Chapter 4). It was also found that in other cases any other 'dips' and 'plateaux' were associated with drifting and therefore useless for this purpose.

The reference electrodes which find greatest use today are the saturated and 3.5-3.8 M KCl calomel electrode. Such electrodes which incorporate a salt bridge are subject to changes in the liquid junction potential due to variations in the ionic strength of the solution under investigation and consequently the potential is not truly invariant. There is obviously, therefore, a demand for an alternative system.

Ideally, the potential of a reference electrode should not vary with pH , however, a low response would be acceptable providing it is reproducible and linear. It is unlikely that a workable reference electrode could be produced in this way, since this would require an electrode to behave in a non-theoretical manner reproducibly. For these reasons the investigation was redirected towards the production of an indicator electrode with a near theoretical response.

Not surprisingly, most of the research on metal-metal oxide electrodes has been directed towards the production of indicator electrodes with Nernstian response. However, to date, no electrode has been found with theoretical pH response over the entire scale. The antimony electrode has received the greatest attention in the past although bismuth and tungsten and other metal electrodes have been investigated by some authors (see Chapter 4 and reference 5).

Another possible use for metal-metal oxide electrodes, discussed by Malmstadt and Fett,[6] is as an indicator electrode to follow titrations. The glass electrode does not respond instantaneously to changes of pH in solution, consequently, the titrant flow rate has to be relatively slow to prevent overshooting the equivalence point, or a blank correction has to be applied in order to correct for any delay in electrode response. The above workers have found that rhodium and certain rhodium-platinum alloys are "ideal" for acid-base automatic differential potentiometric titrations. It should be pointed out, however, that a comparatively slow titrant flow rate is normally essential, in any case, in order to ensure adequate mixing.

Further applications have also been reported. The use of

Pt-metal oxide electrodes as sensors in complexometric titration has been reported by Hulanicki and Trojanowicz[7] and others. In addition, some metal electrodes including antimony and bismuth have been evaluated for non-aqueous potentiometric titrations by Greenhow and Al-Mudarris.[8]

Generally, metal-metal oxide electrodes have been found to be most useful in systems where extremes of alkalinity and temperature would cause the failure of glass or quinhydrone electrodes. They have also been used to replace the hydrogen electrode in cases where the hydrogen electrode would be poisoned or where the passage of hydrogen might remove wanted volatile constituents.

Metal-metal oxide electrodes may be regarded as electrodes of the second kind. The primary electrode process would therefore, in the case of antimony, for example, be the reduction of Sb^{3+} ions to the metal.[1,2] However, an equilibrium is set up, in solution, between the Sb^{3+} ions and hydrated antimony oxide, and it is impossible to remove these ions without affecting this equilibrium,

$$Sb_2O_3 + 6H^+ \rightleftharpoons 2\ Sb^{3+} + 3H_2O \qquad 1.6$$

The complete electrode process is:

$$Sb_2O_3 + 6H^+ + 6e \rightarrow 2\ Sb + 3H_2O \quad (E^\circ = 0.152\ V) \qquad 1.7$$

The ratio of hydrogen ions to electrons is unity and, therefore, the pH response of the antimony electrode would be expected to be similar to that of the hydrogen electrode, the potential being

given by:

$$E = E^{o} - \frac{2.3026\ RT}{F} \cdot pH. \qquad 1.8$$

In practice, it is found that, as one progresses from acid to alkaline solutions, the form of antimony in solution changes through an overlapping series: Sb^{3+}, $SbOH^{2+}$, SbO^{+}, SbO.OH, SbO_2^-, $Sb(OH)_4^-$. However, this is not significant, providing equilibrium exists with the same solid phases, i.e. Sb and Sb_2O_3.

The essential properties of the solid phases for a successful metal-metal oxide pH electrode were listed by Ives and Janz[5] as follows:

The metal must be sufficiently noble to resist direct attack by solutions. Its standard electrode potential (Stockholm convention) should be positive so that the reaction:

$$M + 2H^{+} \rightarrow M^{2+} + H_2 \qquad 1.9$$

has no tendency to occur, otherwise contamination of solution and incorrect pH response, at lower pH values will result.

It must be available in a reproducible state of minimum free energy, not occurring in different polymorphic forms and not being sufficiently hard to have suffered strain or tempering effects from previous treatments.

The oxide phase must be stable and in a reproducible standard state. If the metal has more than one valency, there is a danger that there may be more than one oxide phase present and the electrode potential is unlikely to be controlled by a single reaction. Also, the various oxides may exist in different crystalline forms and this could affect the potential of the electrode.

The oxide should be sparingly soluble so that it does not lead to contamination of the solution. However, at the same time, it must be able to participate without undue hindrance in the equilibria which control electrode potential.

If the potential is to be controlled by a single well-defined, freely occurring process it is essential that the solid phases must be present in adequate amounts and that the ions involved are at sufficient but not too high concentrations. If the latter are not present in sufficient concentrations, it will become impossible for the ions to control the electrode potential. In that case it is likely that the potential will be unstable and will be at the mercy of dissolved oxygen and other impurities[10] (see section 6.1.5).

In general, pH electrodes should have the following characteristics:

1. Easy reproducibility.
2. Small temperature coefficient.
3. Reversibility when current is drawn.
4. Must not deteriorate with time.

It was mentioned previously that a rapid response would be useful for titration experiments. This is also essential if the electrode is to be used for continuous monitoring of processes.

This investigation was begun by the examination of three well-tested systems, the antimony, bismuth and tungsten electrodes (Chapter 4). This was then extended to cover massive noble metal electrodes which received only a small amount of attention in the past (see section 5.1). Finally, Chapter 6 is devoted to the evaluation of a novel electrode system, based on

the electrodeposition of rhodium. In that chapter, both the pH response and certain other aspects of this electrode are investigated.

The detailed description of the preparation of the various metal-metal oxide electrodes used in this work is discussed in the relevant chapters, however, it is useful, at this point, to mention techniques for the construction of electrodes of this type. The methods available for this purpose can be summarized as follows:

1) Chemical Preparation of Oxides.
2) Chemical Preparation in Situ.
3) Electrochemical Methods.

1) Chemical Preparation of Oxides.

Although not used in this investigation some antimony-antimonous oxide electrodes have been prepared from mixtures of finely divided metal and powdered oxide.[5] This type of electrode is not particularly useful for general pH measurement because it tends to be cumbersome to use. A simple stick electrode constructed by methods 2 or 3 would obviously be far more convenient.

2) Chemical Preparation 'in Situ'.

Two forms of 'in situ' oxidation have been employed in this investigation. In the case of reactive metals, air oxidation or oxidation by dissolved oxygen can often be sufficient to form a substantial oxide film. In this investigation, this simple form of oxidation was employed for antimony, bismuth and tungsten electrodes. For the massive, noble metal electrodes a more powerful oxidation procedure was necessary. In most cases, this was

accomplished using fused potassium nitrate, although for gold and, on some occasions, rhodium, electrochemical methods were used.

3) Electrochemical Methods.

In the cases quoted above potentiostatic anodic polarization was employed. Constant current polarization was not employed because it is virtually impossible to ensure that only one oxide species is formed when using this technique. A special technique, whereby an oxide is deposited simultaneously with the rhodium metal, is used in Chapter 8 and is discussed in detail in the first part of that chapter.

Chapter 2

APPARATUS

2.1 pH measurement

Before examining the pH response of metal-metal oxide electrodes, the pH of the test solution must first be determined. In this case, this was done by making use of the glass-calomel cell.

Glass | Experimental soln. || Sat. KCl | Hg_2Cl_2 ; Hg

The potential observed is related to the pH of the solution by the Nernst equation as follows:

$$E_g = E_g^{o} + 0.0592 \log C_{H^+} = E_g^{o} - 0.0592 \text{ pH at } 25^{o}C \qquad 2.1$$

Since the object of this research is to develop an alternative to the glass electrode, clearly it is undesirable to use that electrode for pH measurement in this investigation. However, under the conditions involved in the major part of this investigation, the adverse conditions mentioned previously are not encountered.

The glass electrode was chosen for pH measurement in this investigation because of its availability and the convenience associated with its use. The only other realistic alternative would be the hydrogen electrode. This was ruled out however, because of inherent inflexibility of this system, and the fact that

extremely accurate readings were not required. Also this electrode is far more susceptible to interferences than the above. The merits or otherwise of various pH indicator electrodes were discussed in the last chapter. The glass electrodes employed in the major part of this work were types G202B and G202C manufactured by Radiometer. The 'C' type electrode is more robust, but can only be used for measurements from pH 0-12. The 'B' type electrode is more suitable for measurements from pH 0-14. Below 20°C, the 'B' type gives a slow response. However, since most measurements were carried out at or above this temperature the 'B' electrode was preferred in most cases.

The reference side of the pH measuring cell was fulfilled by the inclusion of a Radiometer K401 saturated calomel electrode. In this form of electrode, a composite of mercurous chloride and mercury is kept in contact with the test solution by means of a saturated KCl salt bridge. Like the glass electrode, this electrode is not without problems (see Chapter 1 and reference 11). However, it may be considered adequate for the appraisal of a new electrode in cases such as this. The potential of this half cell is given by Ives and Janz[12] as 244.4 mV at 25°C.

In the section of this work concerned with the oxygen response of a particular electrode system, the glass-calomel cell was replaced with a Jena Glass combination electrode for reasons associated with the construction of a compact sealed glass 'cell'. This electrode combined a 'Thalamid' reference electrode with a compatible glass electrode. The trade name Thalamid refers to the Thallium amalgam-thallous chloride reference electrode system which is constructed as follows:

$$KCl\ (sat.),\ TlCl\ (sat.)\ \Big|\ TlCl\ (s)\ ;\ Tl(Hg)^{11}$$

Owing to the high resistance of the glass electrode it is necessary to utilise a measuring instrument designed for the purpose. Also in this case, since polarization is a problem likely to be encountered with metal-metal oxide electrodes, it is clearly desirable that the current drawn when measurements are being taken should be infinitesimal, the most obvious instrument to satisfy these conditions would of course be a pH meter. However, the Mettler titrimeter (DK10/11,12) chosen for this investigation widens the choice of experimental techniques available when used in conjunction with the Mettler digital burette (DV10) and the Mettler pulse stepping recorder (GA 10). The actual experimental methods employed will be dealt with in detail in the next chapter and a comprehensive calibration of the Mettler instrument is given in Appendix (1). A digital facility was incorporated in the apparatus by the inclusion of a Fenlow digital voltmeter (Type 701).

The calomel electrode was used as a common reference electrode, while selection between glass and test electrodes was achieved by means of a shielded 'break before make' switch. This sequence was necessary to eliminate errors resulting from short circuiting the various measuring electrodes. All the electrode connections, apart from that to the calomel electrode were made with shielded, non-microphonic cable, the shielding being earthed, as was the calomel electrode itself. Stirring was accomplished, in most cases by the slowest rate available on a Radiometer type M24 stirrer (paddle type); although in some of the later

experiments this was replaced by a magnetic stirrer. A schematic diagram of the potential measuring apparatus is given in figure 2.1.

Most of the early experiments of this work were carried out using an open vessel without temperature control. Since the electrodes were intended for industrial use, it was not considered desirable for the experimental conditions to be controlled in the initial assessment of the various electrodes. It was soon found that variations in laboratory ambient temperature were too great so that the control of temperature, in particular, was necessary in order to obtain accurate results. This was achieved through the use of a Tecam 'Tempunit' and a water bath.

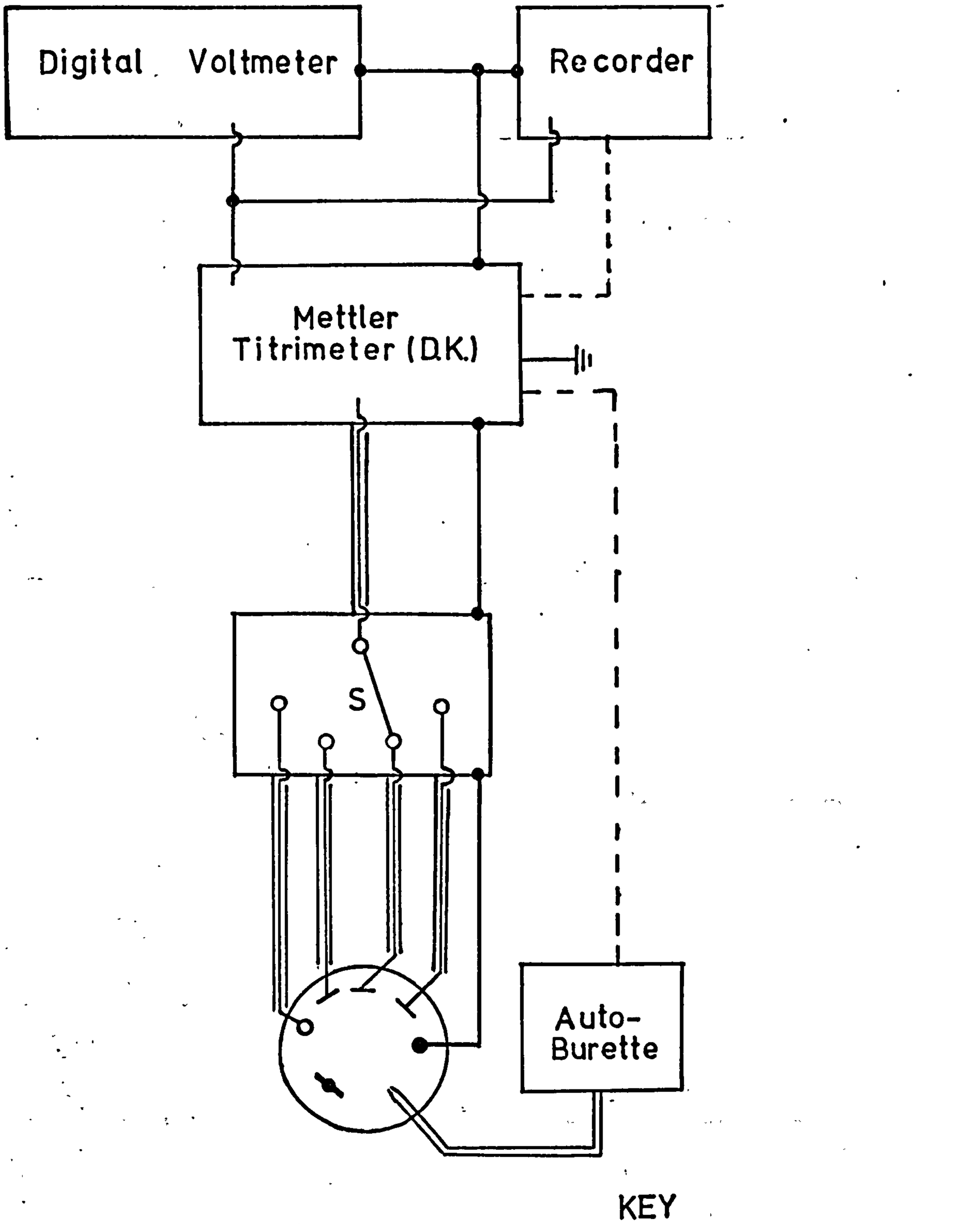
2.2 Variation of oxygen partial pressure

This was achieved by passing streams of oxygen and nitrogen through separate flow meters (Rotameters). The partial pressure of oxygen and hence the concentration in solution may be determined from the ratio indicated on the two meters. A six-inch length of capillary tube was incorporated in each arm in order to prevent a 'pressure surge' and thus facilitate the adjustment of the flow rates (see fig. 2.2) and reduce the possibility of a blowback.

Mixing was achieved by means of a simple glass Y-piece. Clearly a special mixing vessel would be preferable but, since a high degree of accuracy was not required, this was not deemed to be necessary. Before entering the vessel containing the solution, the gas mixture was first passed through a 'bubbler' containing distilled water in order to saturate the gas with water vapour.

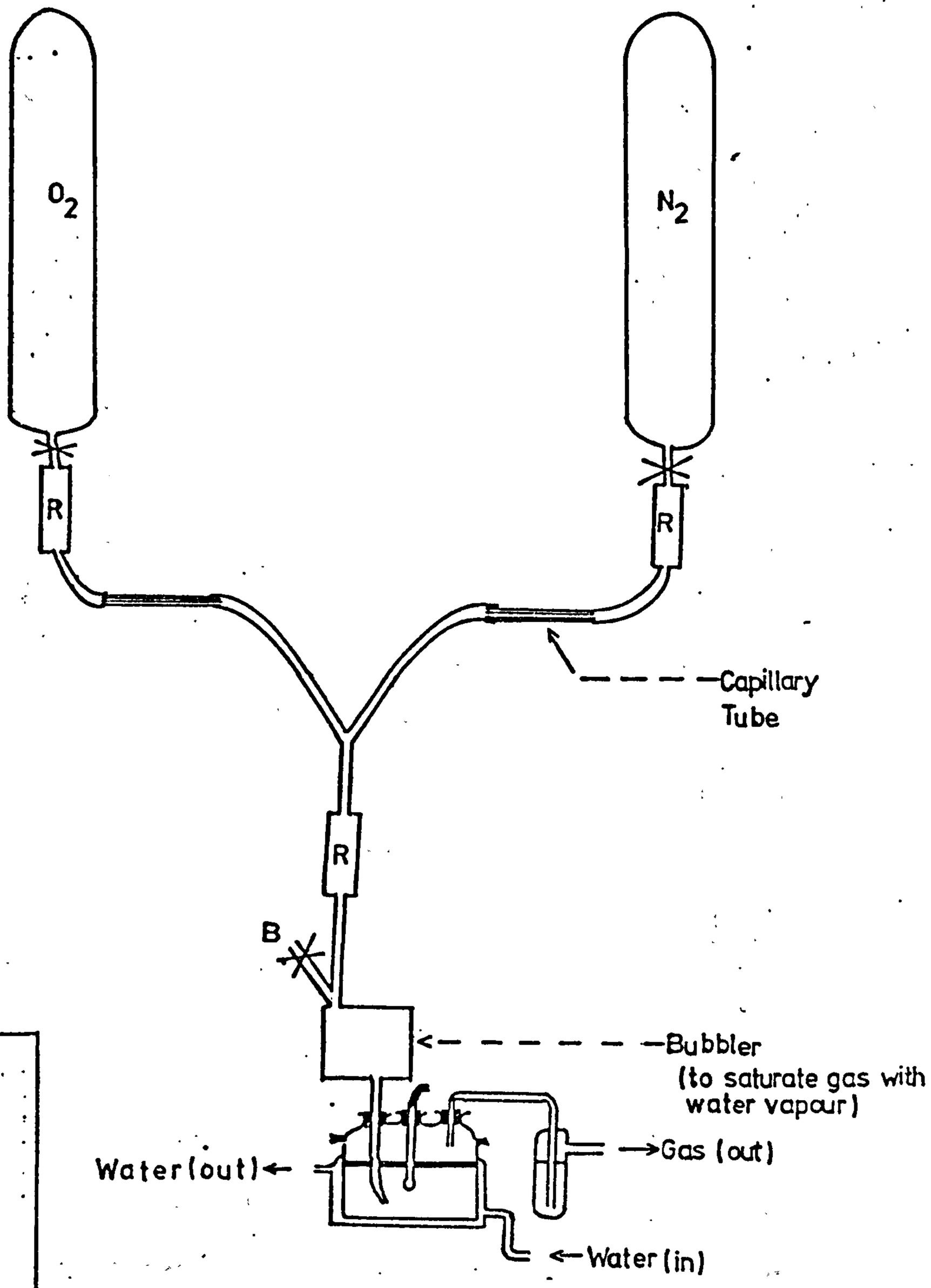
FIG. 2.1

SCHEMATIC DIAGRAM OF POTENTIAL MEASURING APPARATUS



SCHEMATIC DIAGRAM OF THE APPARATUS USED FOR TAKING MEASUREMENTS UNDER CONTROLLED OXYGEN PARTIAL PRESSURES

FIG. 2.2



KEY

R ....Rotameter

B.....Gas-bleed

If this was not done the gas would tend gradually to remove water from the solution, thus changing its concentration.

Since a comparatively large volume of gas is required to operate the Rotameters (R) a gas bleed B was incorporated in the apparatus in order to enable the gas mixture to be passed at a reasonable rate through the solution. The third Rotameter was included as a reference for the other two flow meters. This was done in order to enable the observed O_2/N_2 ratio to be corrected for any discrepancies in the individual meters.

A reasonably air-tight vessel was constructed in two parts. The lower section had an outer jacket so that water at a constant temperature could be passed through from a water bath and Tempunit. The upper section was fitted with ground glass sockets for the various electrodes, thermometer and inlet and outlet pipes. The two sections were joined by means of a flat ground glass flange and held together by spring clips. Finally the gas mixture is vented to the atmosphere via a distilled water bubbler. The latter segregates the atmosphere in the vessel from the external environment and the levels of the two menisci provide a useful indication as to the airtightness or otherwise of the apparatus. Stirring was effected in this case by means of a magnetic stirrer.

2.3 Calibrations

Calibrations of the Mettler Titrimeter recorder and Fenlow D.V.M. were accomplished using a Precision Potentiometer Type 4580 which was in turn calibrated against a 'Weston' cell at 1.0186 V ($20^{\circ}C$). The full calibration procedure for the pH meters is given in the Appendix along with the calibration for this instrument.

Chapter 3

EXPERIMENTAL TECHNIQUES AND PREPARATION OF SOLUTIONS

3.1 Experimental techniques

The techniques available to the experimenter in investigating the electrode reponse to pH variation are strictly limited. Essentially, all that is required is a means of changing the pH of the solution to which the electrode under examination is subjected. The available techniques may be summarized as follows:

(1) Transfer between individual solutions

(2) Titration techniques

(a) incremental

(b) continuous

3.1.1 Transfer techniques

Transfer techniques involve the manual removal of the electrodes from one solution to another and examining the resultant effect on the electrode potential. The steady E.M.F. values obtained from a number of solutions are then plotted against the corresponding pH values obtained from the glass-calomel cell. In this investigation, this technique was limited in most cases to inorganic salt solutions.

This technique suffers from the disadvantage that cross-

contamination or dilution may occur during transfer, however, a more serious disadvantage is encountered in the assessment of metal-metal oxide electrode systems. This relates to possible effects of ionic strength, oxygen concentration and other factors which are difficult to control in individual solutions of varying composition. Oxygen concentration is particularly important since various electrolytes are known to have a pronounced effect on the solubility of this gas in water. Another relevant disadvantage is the possibility of spurious electrochemical effects due to the removal of the electrodes from solution. These problems can be alleviated to a certain extent by the use of titration techniques.

3.1.2 Titration techniques

This term embraces two similar methods as indicated above. Unlike the transfer technique only one solution is employed to cover a wide range of pH values. A solution suitable for this purpose has to be specially formulated so that it is buffered over the entire pH range. Solutions such as this are known as Universal Buffers and are discussed in detail later in this chapter.

In its simplest form, referred to in this work as 'incremental' or stepwise titrations, aliquots of acid or alkaline solution are run into the universal buffer solution so that the pH of that solution is altered by say, 1 or 2 pH units. The response of the electrode to the pH change is then monitored in the same way as for the transfer technique.

Since the composition of the solution apart from H^+ concentration is substantially unaltered during the entire experiment,

the oxygen concentration and ionic strength remain relatively constant. Also since the electrode is exposed to the same solution throughout the entire experiment, problems arising from the removal of the electrodes from solution and transfer between solutions are eliminated. Like the transfer technique this method enables the behaviour over long periods of time to be examined. This is particularly important if the electrode is intended for the direct measurement of pH or for the continuous monitoring of stagnant or flowing electrolyte solutions.

An adaptation of the above method utilizes the special facilities of the Mettler instrument which enables solutions to be run into the buffer solution at a constant rate in a manner analogous to automatic acid/base titrations. However, in this case the composition of the universal buffer is selected such that the pH/volume plot is as close to linearity as possible. If some volume of an identical solution is used in each case, after an initial glass calomel titration has been carried out to determine the pH/volume relationship, the procedure can be repeated for a large number of electrodes with no further calibrations. This method has the advantage of being relatively rapid and so is useful as a tool for the initial appraisal of electrodes. Another advantage of this method lies in the fact that it enables an assessment of the immediate response of an electrode to be made. Since the pH change is comparatively rapid. if the electrode has a slow response, the observed potential pH slope will be lower than expected. This method is particularly useful if there is a pronounced drift superimposed over the initial/pH change. Simple acid/base titrations may also be considered as a suitable technique

for the assessment of pH electrodes.

3.2 Preparation of solutions

During the course of this investigation a number of different aqueous solutions, both buffered and unbuffered, have been employed. Unbuffered solutions have the disadvantage of being particularly susceptible to changes of pH caused by the addition of small quantities of acid or base. For this reason, it is desirable for unbuffered solutions to be isolated from the atmosphere since the absorption of carbon dioxide can cause pronounced drifts in pH . Changes in concentration of the solution are equally undesirable. For these and other reasons, electrode potentials obtained from unbuffered solutions tend to be variable and suffer greatly from electrical noise. To avoid these difficulties, in most instances, potential-pH measurements are made under buffered conditions.

One of the cases where the use of unbuffered solutions is permissible is that of titration. In this technique, the experiment is completed so rapidly that there is insufficient time for the above disadvantages to be of any consequence. Unfortunately, the amount of information obtainable from this technique is very limited.

The use of unbuffered solutions is also justifiable in the case of strongly acidic or basic solutions which exhibit very little change in pH when acid or alkali is added. These are described by Perrin and Dempsey,[13] as "pseudo buffers". In solutions such as these the 'buffering' action is due to the solvent rather than

the solute, therefore it would be incorrect to refer to them as buffers.

Although a wide variety of compounds is available as buffer substances over much of the pH scale, very few are available from pH 6 to 9.[14,15,16,17] Until fairly recently the few buffers available in this physiologically important region were quite unsuitable for this purpose. This unfortunate gap has now been filled by a long list of very similar amine buffers.[14,15,17,18]

Amine buffers were chosen for much of the work reported in this thesis mainly in order to eliminate small ion interferents from the vicinity of the metal-metal oxide electrodes. Also, as mentioned previously, it is possible that electrode systems of this kind may find use in biological or biochemical applications where buffers of this sort might be encountered.

The buffer substance chosen for use in the pH range 7 to 9 was tris (hydroxymethyl) aminomethane.[15,16] The pK of this material, which can be described as the mid point of its buffering range, has been quoted as 8.06 at 25°C.[18] This material, which is normally referred to by the trivial names of Tris or THAM, has the formula $(CH_2OH)_3C.NH_2$.

Although measurements can be made outside the buffered range, Tris has a poor buffering capacity below pH 7.5 and consequently Bis-tris was chosen for the pH range 5.5 to 7.5.[16] This base, which has the systematic name bis-(2-hydroxyethyl)imino -tris (hydroxymethyl)methane ,[18] has a pK of 6.46 at 20°C[18] and the formula $(HO.CH_2.CH_2)_2.N.C.(CH_2OH)_3$.

At one stage in this investigation it was found to be necessary to replace bis-tris with another comparable buffer (see

Chapter 7). For this purpose, a buffer with a pK of 7.17 at 20°C was chosen,[18] namely BES or N,N-Bis(2-hydroxyethyl) -2-amino-ethanesulphonic acid. This has the formula: $(HO.CH_2.CH_2)_2.N.CH_2.CH_2.SO_3H$.

Of course, the use of amine buffers cannot be extended to lower pH values because of their nature. Therefore, in order to preserve the continuity of the buffer system, the pH range 3 to 5.5 was covered by the titration of succinic acid with tetramethylammonium hydroxide, hereafter referred to as T.M.A.H. Since succinic acid has two pK values at 4.21 and 5.64[18] at 25°C, this material makes an almost ideal buffer system. In the case of Tris and Bis-tris, variation of pH within the buffered zone was achieved by titration with hydrochloric acid.

Another amine buffer, ethanolamine, was also utilized, but the use of this material was confined to the latter part of the investigation. This compound, $HO.CH_2.CH_2.NH_2$ has a pK of 9.50[18] and can be used to buffer in the pH range 8.5 to 10.5.[15]

As can be seen from the corresponding values, each of the materials mentioned above can be used for buffer solutions varying in pH by as much as 2 pH units. It is, therefore, possible to use these materials as 'wide' range buffers in their own rights. In this investigation, for instance, Tris, Bis-tris and tetramethyl-ammonium succinate were used for individual buffer solutions in the assessment of the antimony electrode. In the case of Bis-tris and Tris, the pH was varied by means of the addition of aliquots of aqueous hydrochloric acid. In the case of T.M.A.H./succinic acid a method of changing the pH is, of course, built into the system.

As was indicated in a preceding section of the chapter, it is desirable for this work that the pH of a buffer solution should be variable over a wide range. Although this is possible to a limited degree with individual buffer substances (as shown above), the only way that a solution can be buffered over the greater part of the pH scale is by making use of a universal buffer mixture.

The term universal buffer is the name given to a solution made up from a mixture of individual buffer substances, formulated in such a way that their buffered zones overlap. Britton and Robinson[19] infer from theoretical considerations that the ideal mixture, giving an absolutely straight line when titrated with alkali, should consist of weak acids whose respective pK values differ from one another by 1.2. These authors also deduce that, at the mid-point of any stage in the neutralization pH should be equal to the pK of the appropriate acid and at the end of one stage and the beginning of another the pH should equal half the sum of the pK's of the acids concerned.

The concept of universal buffers is not new as mixtures of this sort were reported as early as 1921, and at least six different mixtures are listed in reference 13. In order to determine the most suitable universal buffer for our purposes, a number of established mixtures were titrated using the Mettler instrument and compared to specially fabricated mixtures. The established buffer systems chosen for examination were those suggested by Mellon et al. (1921),[20] Prideaux and Ward (1924),[21] Britton and Robinson (1931)[19] and Best and Samuel (1936).[22] The components of the various systems and the concentrations used are listed in the accompanying table

Table 3.1

ESTABLISHED UNIVERSAL BUFFERS (50 cm^3)

Source	Components	Concentration	Titrant
Prideaux & Ward I.B.1	Phosphoric acid Boric acid Phenylacetic acid	0.02 N w.r.t. each hydrion (0.1N Total)	0.5 M NaOH
Best & Samuel I.B.2	Potassium Dihyd. Phosphate, Potassium Hyd. Phthalate, Boric acid.	0.0533 M w.r.t. each compound.	1.0 M NaOH
Britton & Robinson I.B.3	Boric acid, Citric acid, Barbitone(Na salt) Potassium Dihyd. Phosphate, HCl	0.0286 N w.r.t. each component. $1.4cm^3$ 1M	1.0 M NaOH
Mellon et al. I.B.4	Sodium acetate, Sodium formate, Phenolsulphonic acid, Potassium Dihyd. Phosphate. HCl	0.04 M 0.04 M 0.04 M $3cm^3$ 1M	0.5 M NaOH

(Table 3.1). The corresponding titration results are given in figures 3.1, 3.2, 3.3 and 3.4. Two possible buffer mixtures were rejected on various grounds. The mixture suggested by Ellis[23] was avoided because of difficulties associated with the composition of the mixture, while the mixture proposed by Carmody[24] was rejected on the grounds that this buffer system was intended to be made up as individual solutions, varying the composition of both components rather than merely running in an alkaline solution to a fixed volume of universal buffer. Also, in the latter case, the component chosen as the titrant (trisodium orthophosphate) was found to be incompatible with the Mettler automatic burette.

The universal buffer mixture put forward by Prideaux and Ward[21] was composed of orthophosphoric acid, boric acid and phenylacetic acid. Since phosphoric acid has three neutralization stages, it will have three corresponding pK values, which are 2.15, 7.20 ($20^{o}C$) and 12.33. (In the remainder of this chapter, unless otherwise indicated the pK values quoted refer to $25^{o}C$ and are taken from reference 18.) Phenylacetic acid and boric acid are monobasic with pK values, respectively 4.27 ($18^{o}C$)[21] and 9.23. It can be seen from the above figures that the differences between the various adjacent pK values vary from 2.03 to 3.13, i.e. well above the suggested figure of 1.2.[19] It is, therefore, not surprising that this investigation yielded a curve which was undulatory in character. This finding is in agreement with that of Britton and Robinson,[25] who adapted the solution used by Prideaux and Ward for making up a series of individual solutions, for use under titration conditions.

The mixture employed by Best and Samuel,[22] consists of boric

FIG. 3.1

CONTINUOUS TITRATION OF I.B.1 (50 cm^3)

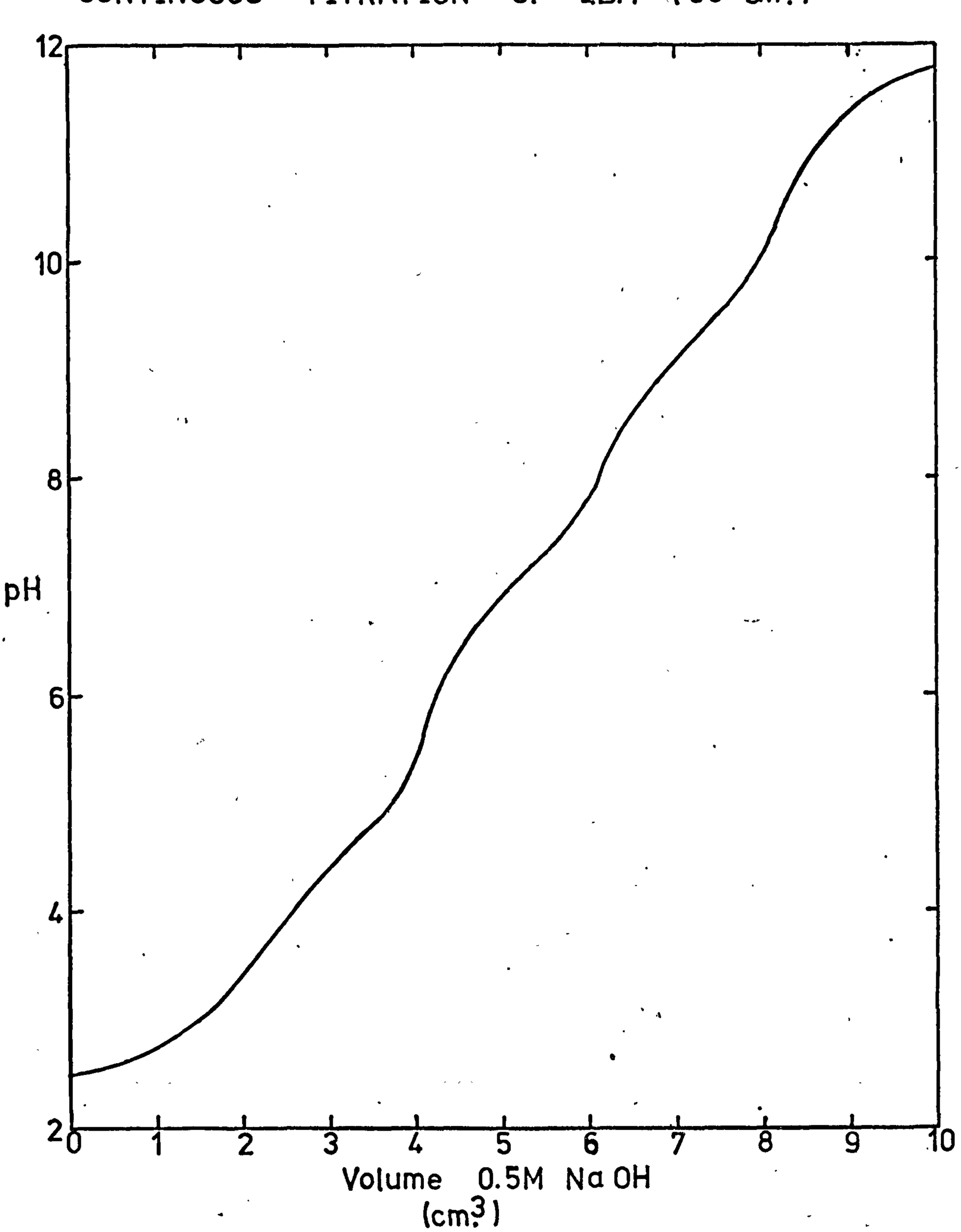


FIG. 3.2

CONTINUOUS TITRATION OF I.B.2 (50 cm^3)

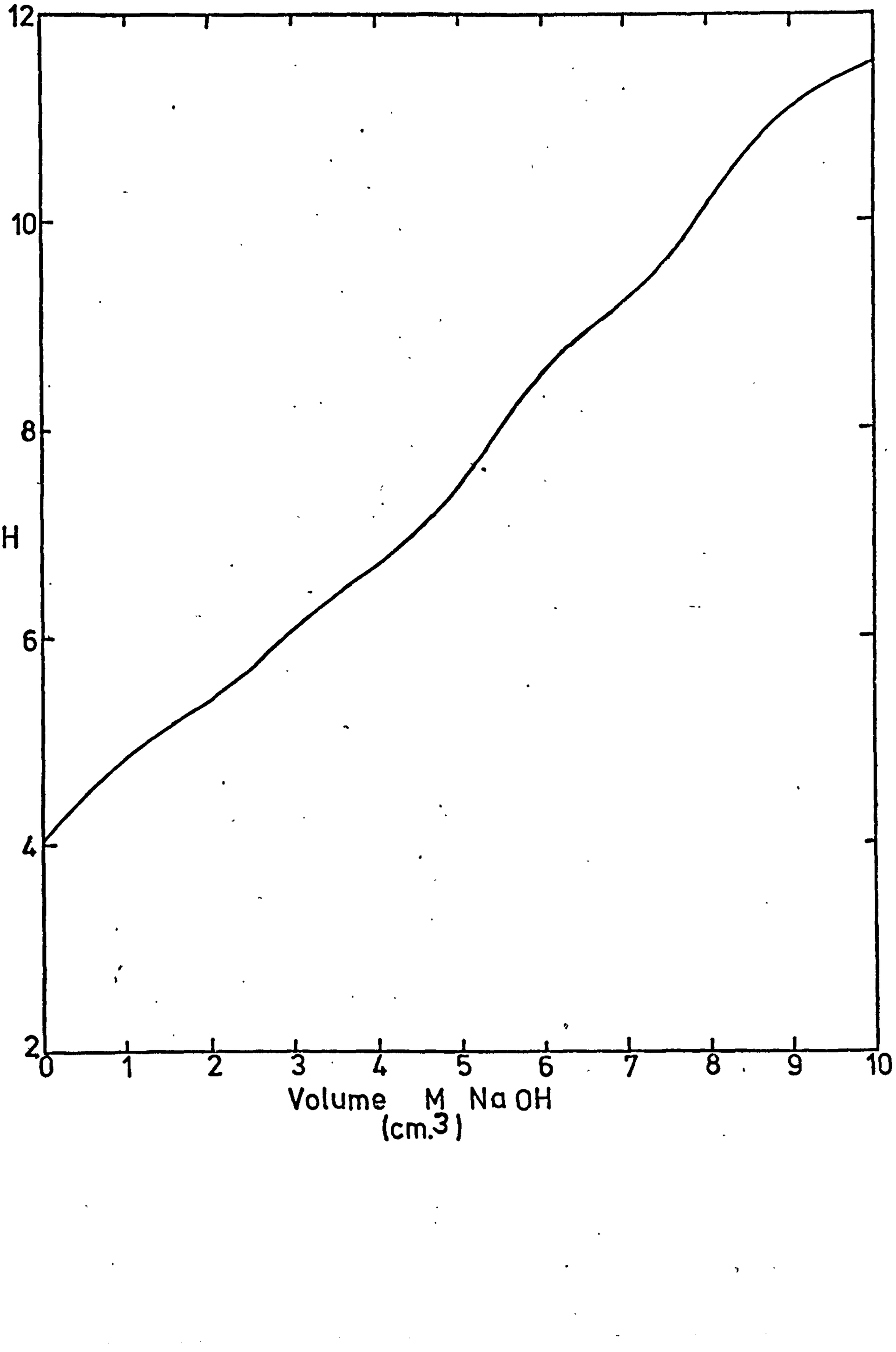


FIG. 3.3

CONTINUOUS TITRATION OF I.B.3

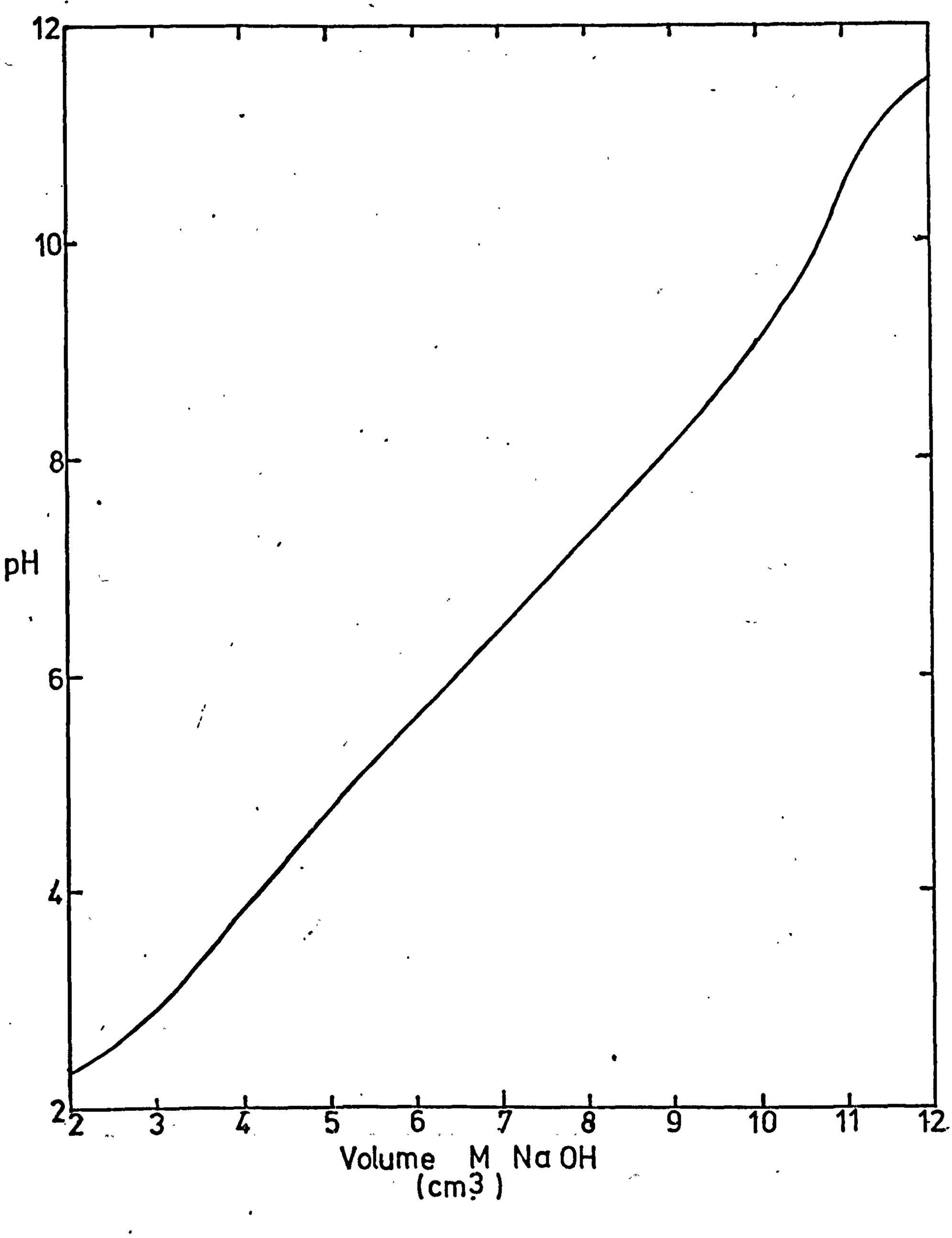
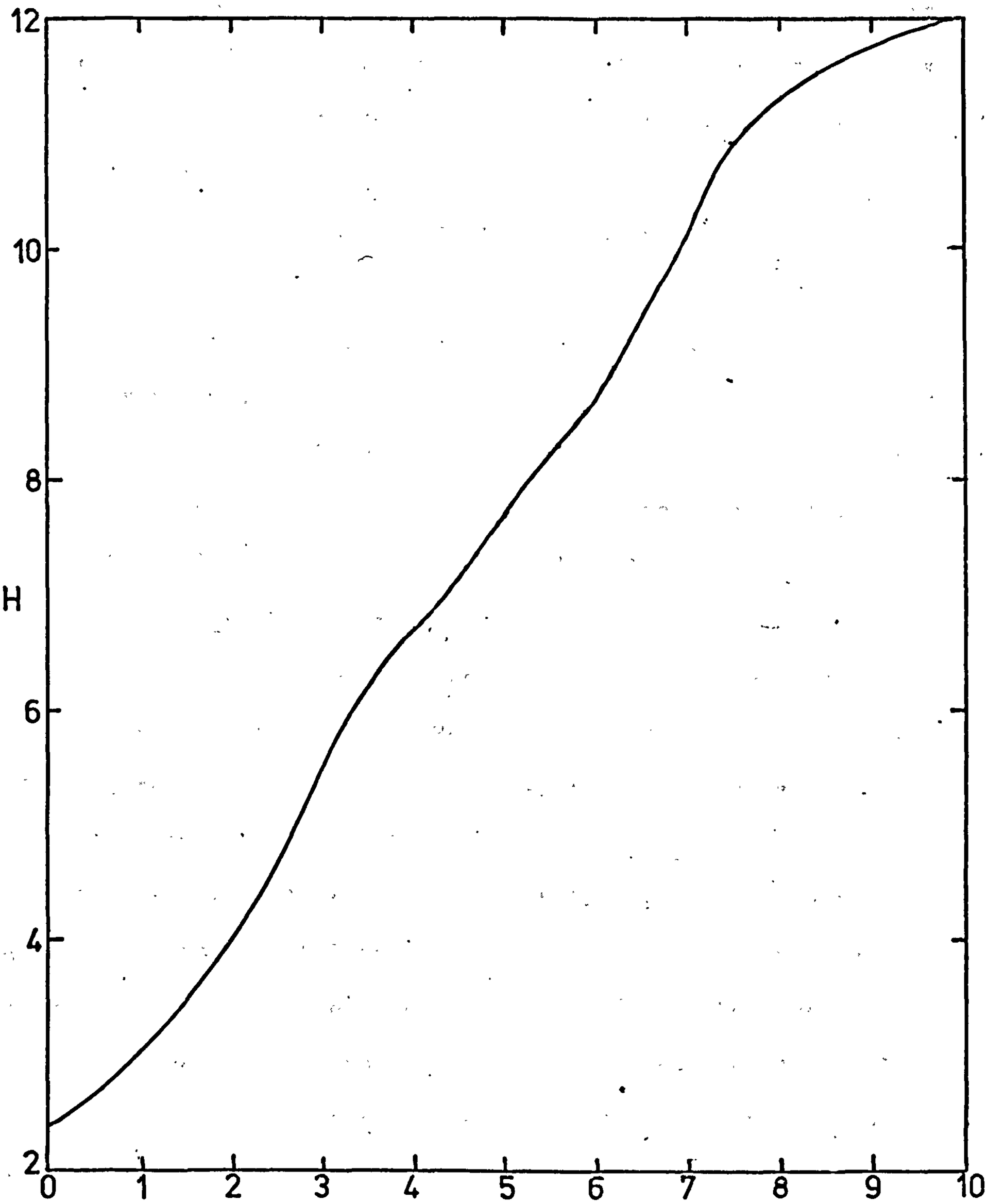


FIG. 3.4

CONTINUOUS TITRATION OF I.B.4 (50 cm^3)



acid, potassium dihydrogen phosphate, and potassium hydrogen phthalate (Table 3.1). The pK values associated with the first two components are as quoted above. Potassium hydrogen phthalate, a salt of a dibasic acid, has pK values of 2.95 and 5.41. When titrated, an undulatory curve was again observed. Since over the measured pH range, the pK values are again more than 1.2 pH units apart (1.79 to 3.13), it is reasonable to expect this. As lower pH values are not of great interest to this investigation, it was decided that this mixture would be of little value.

The Britton and Robinson buffer system[19] consists of boric acid, citric acid, potassium dihydrogen phosphate and the sodium salt of 5,5-diethylbarbituric acid, which is sometimes known as barbitone or veronal. Citric acid, like phosphoric acid, has three pK values, at 3.13, 4.76 and 6.40. Veronal on the other hand is monobasic, with a pK of 7.98. The close adherence to a linear pH change below pH9 can be attributed to the close proximity of the various pK values. The large step observed above pH 9 corresponds to a difference of 3.10 between the two relevant pK's.

The final established universal buffer system to be tested was that reported by Mellon and coworkers.[20] This mixture included sodium formate (5/8 mole), sodium acetate (3/8 mole), potassium dihydrogen phosphate (1 mole) and phenolsulphonic acid (1 mole). Thymol was included in the original specification, but it was decided to omit this component in this instance. Formic acid has a pK of 3.75 while acetic acid has a pK of 4.76. 4-phenol-sulphonic acid has a pK of 9.05 and thymol, the excluded

component, has a pK of about 10.30.[20] As would be expected, a straight line was obtained between 2.5 and 4.5. Large steps were observed around pH 5 and 10.5. The first step is probably due to a gap of 2.4 between two pK values, while the step at pH 10.5 is presumably due to the omission of thymol from the mixture.

The mixtures tested by Best and Samuel and by Britton and Robinson were originally formulated with a view to producing solutions of known pH. In this investigation, this consideration is of little or no importance. The ideal mixture, in this case, should give an approximately linear pH-volume plot and should give reproducible pH values within a particular 'batch' of solution. The only universal buffer system to fulfil this requirement was that specified by Britton and Robinson.

As mentioned previously, it was considered desirable to exclude possible small-ion interferents from the solutions used in the initial assessment of the electrodes examined in this investigation. For this reason, the search for a suitable universal buffer was extended to include solutions containing organic bases. The composition of each solution is given in Table 3.2.

Figure 3.5 illustrates the titration curves displayed when U.B.1 and U.B.2 (10 cm^3 diluted by 10 cm^3 water in each case) were titrated with 0.04 M HCl. In the case of U.B.1, the plot obtained was virtually linear from about pH 8.7 to 3.5. The slight step observed around pH 7 would appear to be due to 1.60 gap between the pK values of Bis-Tris and Tris. The disastrous effect of omitting one component is illustrated by U.B.2. In practice this solution was found to be useful in some specific cases (see Chapter 4, for instance).

FIG. 3.5

CONTINUOUS TITRATION OF AMINE UNIVERSAL BUFFERS ($10cm^3$ + $10cm^3$ H_2O)

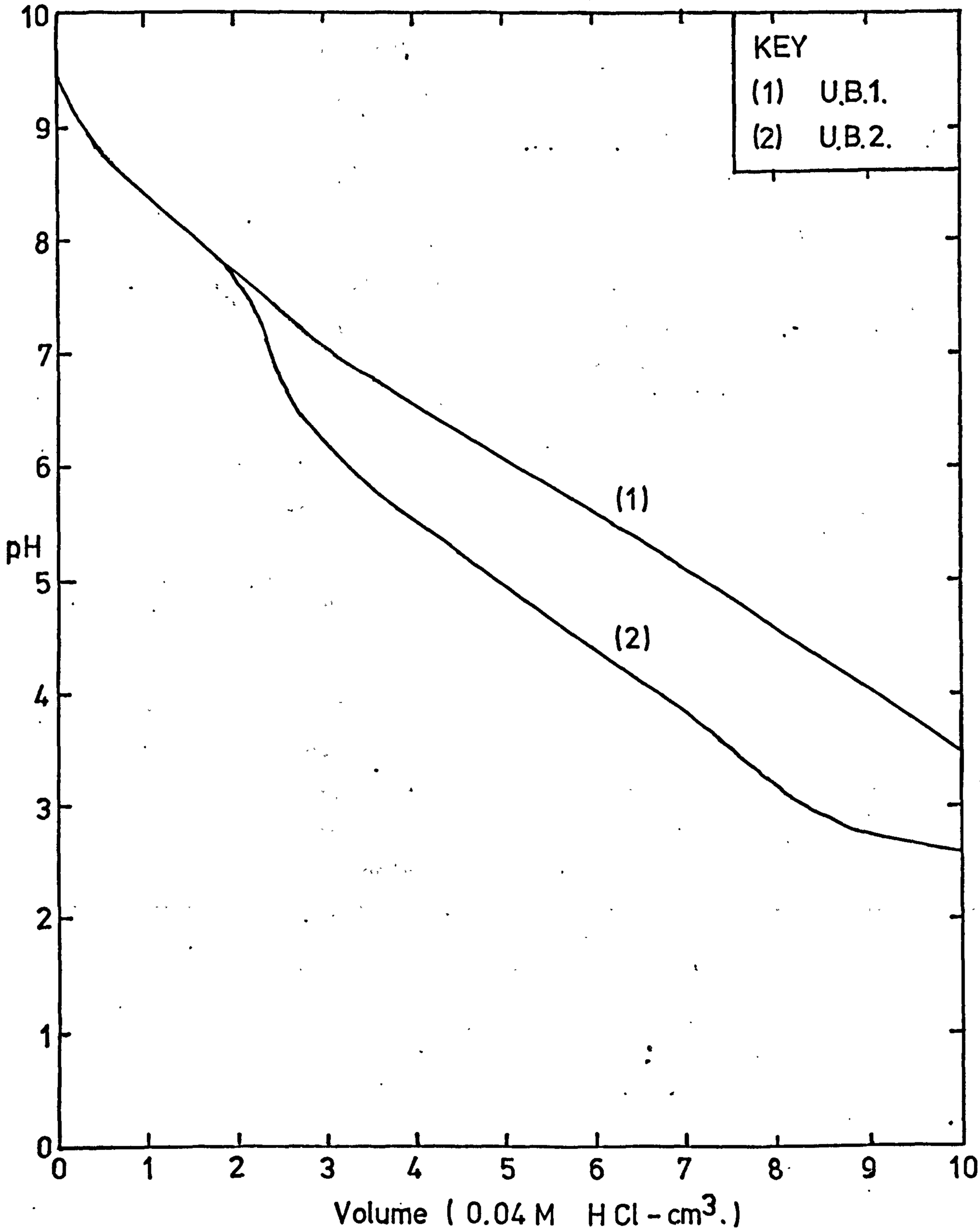
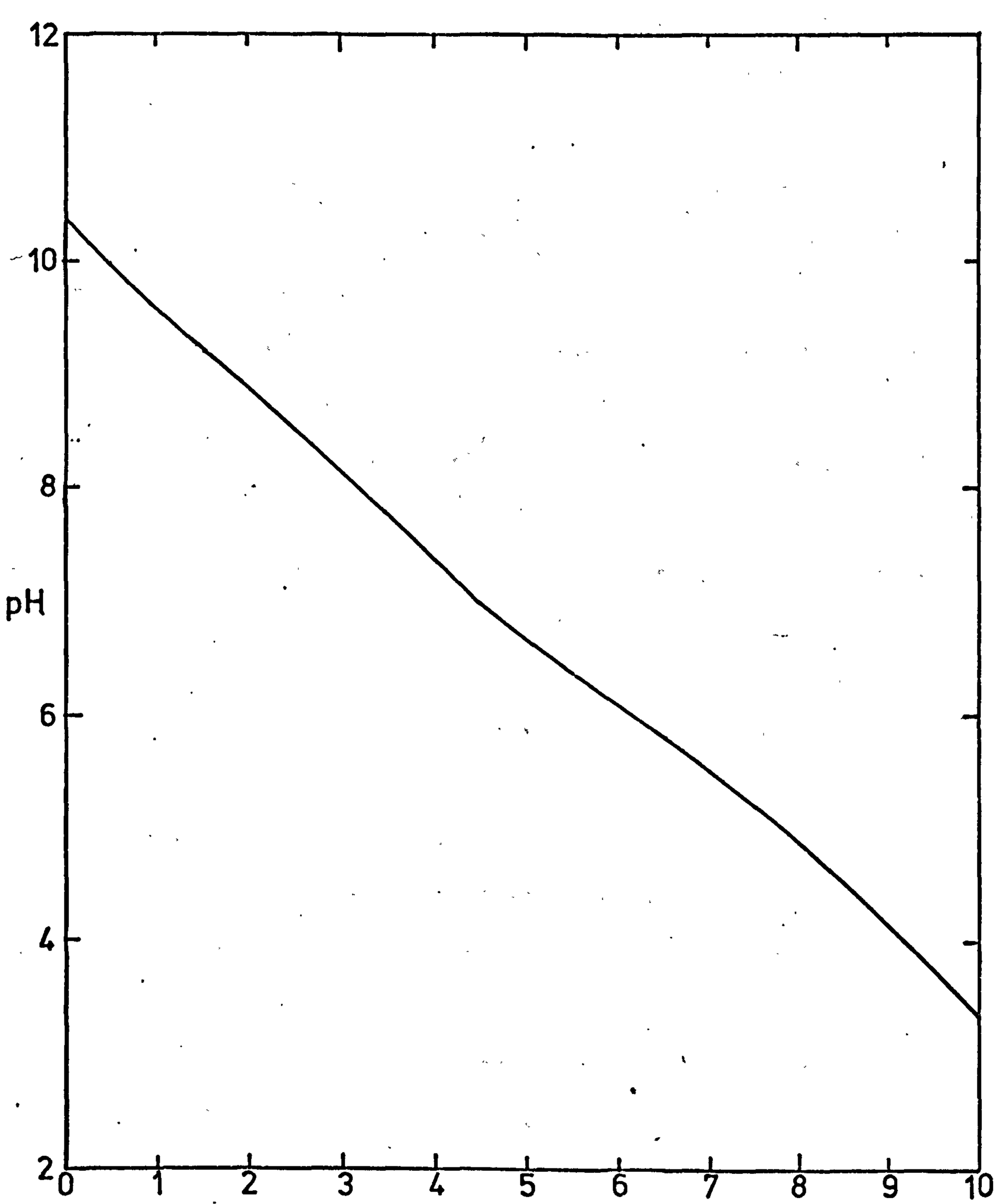


Table 3.2

Nomenclature	Component	Concentration	pK
U.B.1	Succinic acid	0.01 M	4.21, 5.64
	TMAH	0.02 M	
	Bis-tris	0.01 M	6.46 ($20^{\circ}C$)
	Tris	0.01 M	8.06
U.B.2	Succinic acid	0.01 M	4.21, 5.64
	TMAH	0.02 M	
	Tris	0.01 M	8.06
U.B.3	Succinic acid	0.01 M	4.21, 5.64
	TMAH	0.02 M	
	BES	0.01 M	7.17 ($20^{\circ}C$)
	Tris	0.01 M	8.06
U.B.4	Succinic acid	0.01 M	4.21, 5.64
	TMAH	0.02 M	
	Bis-tris	0.01 M	6.46 ($20^{\circ}C$)
	Tris	0.01 M	8.06
	Ethanolamine	0.01 M	9.50

FIG. 3.6

CONTINUOUS TITRATION OF U.B.4 ($20 cm^3$)



When U.B.3 is titrated (not illustrated), it is found, as expected, that the step is displaced to between pH 5.5 and 6. The titration curve obtained from U.B.4 is essentially the same as that from U.B.1 except that the buffered zone is extended beyond pH 10.4. In the case of U.B.4, the illustration relates to the titration of 20 cm^3 of universal buffer with 0.1 M HCl (figure 3.6).

It can be inferred, from the results reported above, that the universal buffers most suitable for use in electrode assessment are U.B.1, U.B.4 and the mixture described by Britton and Robinson.[19] U.B.1 and U.B.4 were used in most instances, although U.B.2 and U.B.3 were found to be useful for special applications. In the event, only one of the established buffer mixtures was used, that described by Best and Samuel.[22] This solution was chosen because of its simple composition and because the absence of complicated organic molecules was found to be desirable for another specialized application (see section 6.1). The use of the buffer solutions under experimental conditions will be described in the relevant chapters.

In addition to the universal buffer solutions mentioned above, a number of individual solutions were used in the course of this investigation. For example, a number of Clark and Lubs[26] mixtures were made up in order to investigate the interferent effect of potassium chloride on the antimony electrode. These are listed in Table 3.3.

Table 3.3

No.	Buffer	Acid or Alkali	Volume (cm^3)
1)	50 cm^3. 0.1 M potassium	0.1 M HCl	(22.3
2)	hydrogen phthalate		(4.5
3)	50 cm^3. 0.1 M potassium	0.1 M $HClO_4$	(22.3
4)	hydrogen phthalate		(4.5
5)	50 cm^3. 0.1 M potassium	0.1 M NaOH	(8.7
6)	hydrogen phthalate		(28.8
7)			(42.3
8)	50 cm^3. 0.1 M potassium	0.1 M NaOH	(13.9
9)	dihydrogen phosphate		(37.0
10)			(46.1

A number of other solutions were used at various stages in this work. These were mainly NBS primary and BS secondary standards,[27] although some other solutions were also employed. These are listed in the relevant chapters.

Finally the day to day calibration of the Mettler titrimeter was carried out using two standards namely potassium hydrogen phthalate (0.05m) and a mixture of potassium dihydrogen phosphate (0.025 m) and disodium hydrogen phosphate (0.025 m). In some cases specially formulated buffers were made up (Tris/HCl and Bis-tris/HCl) in order to avoid the introduction of metal ions into the experimental vessel. The two primary standards quoted above have pH values of 4.008 and 6.865 at 25°C.

The buffer substances employed in this investigation, with

the exception of Tris and Bis-tris, were of Analar quality and supplied by British Drug Houses. Tris solutions were made up from a sample (PURISS) obtained from Koch-Light Laboratories while Bis-tris solutions were prepared from a sample supplied by the Aldrich Chemical Company. All solutions were made up using distilled water.

Chapter 4

ANTIMONY, BISMUTH AND TUNGSTEN ELECTRODES

In this chapter, three electrode systems have been examined namely: antimony, bismuth and tungsten. The chapter has been divided into two main sections, an introduction in which the previous work on the system has been summarized and an experimental section which is further subdivided into sections concerned with electrode construction and solutions employed other than those dealt with in Chapter 3.

4.1 Introduction

4.1.1 Antimony-Antimonous Oxide Electrode[5]

The antimony electrode has been the subject of a number of investigations. Although widely used for a number of years it has now fallen from favour and has been replaced in most cases by the glass electrode. It is still used for certain applications where its small size is advantageous. The possibility of producing extremely small electrodes makes this system particularly attractive for use in medical applications such as the monitoring of the pH of urine in renal tubules.[28]

One of the reasons for this fall from favour is the apparently defective response of the electrode. Most of the results reported in the literature show the potential - pH slope varying from one pH region to another. Tourky and Mousa,[29]

working under air-free conditions, reported a potential - pH plot with breaks at pH 2, 5 and 8. Pronounced deviations from the theoretical response were also reported by Bishop and Short[30] when working with solutions under an atmosphere of pure oxygen, an apparent plateau being visible around neutrality. In general, the values quoted for the slope range from about -50 to -59 mV/pH at 25°C.

Although the potentials of individual electrodes are apparently not very reproducible, a single antimony electrode, (properly calibrated with several buffer solutions) may be used to make satisfactory pH measurements between pH 1 and 10 or to obtain titration curves. The value for the temperature coefficient (2 - 3 mV/K),[2] is rather large for reference purposes.

The E^{o} values assigned to the electrode have varied considerably depending on the authors involved, but two distinct groups are noticeable.[31] It appears that when finely divided metal is used, values approaching the thermodynamic value of 140 mV are obtained. If, however, massive antimony is used, values more positive by approximately 100 mV are obtained. Tourky and Moussa[31] explain this by postulating that the behaviour of the electrode in air is governed by an "oxygen overvoltage effect" due to the persistence, on its surface, of oxygen doublets.

A more satisfactory explanation is given by the concept of a polyelectrode system.[5] A local cell may be set up on the metal surface, in the presence of oxygen, because antimony is an active metal and can dissolve in acid and alkaline solutions.

Sb^{3+} ions would go into solutions at bare metal (anodic) sites, while at protected sites covered with oxides (cathodic sites), a reduction process would take place. The reduction of oxygen would be the most likely process to take place. A local-action current would be expected to flow, within the metal, between the anodic and cathodic sites, thus causing, or increasing, polarization at each of them.

This explanation is supported by the effects of changes in the partial pressure of oxygen and in the rate of stirring.[5,32] An increase in the partial pressure of oxygen causes a positive shift of potential. It can be seen that dissolved oxygen reaching the metal surface will cause cathodic depolarization and cause the oxide film to grow. This will cause the electrode potential to move in a positive direction. The ratio of cathodic to anodic areas will, therefore, be increased causing the onset of anodic polarization which will also displace the potential to the positive side.

When an electrode is immersed in a still, aerated buffer solution a 'positive creep' in potential is observed. When the solution is stirred the potential rapidly falls to a more negative value, (explained by the rapid onset of anodic depolarization). This effect is probably due to the stirrer sweeping away ions produced by anodic dissolution. The stirred solution, however, shows a considerably more rapid positive creep, (due to the slower onset of cathodic depolarization). In this case, the stirrer probably has the effect of bringing up oxygen to the cathodic areas. When stirring is stopped the potential quite rapidly rises to a value more positive than that which

would have been obtained, had the solution not been agitated at all.

The effects of complexing agents, such as tartrates, citrates and oxalates, may be explained as follows. The removal of the oxide film favours anodic depolarization by increasing the anodic to cathodic area ratio. This would then cause a negative shift in potential. Oxidizing agents, on the other hand, would have an opposite effect, causing a positive shift in potential. A large salt error was reported by King[33] who suggested that the presence of potassium chloride was responsible for the changes in slope reported by some authors.

The construction of the electrodes described in the literature falls into three categories: stick electrodes, plated electrodes and powder electrodes. Stick electrodes are cast from molten antimony, to which antimony trioxide may or may not be added. It has been reported that this practice shortens the response time of the electrode. Plated electrodes are prepared by the electrodeposition of antimony on a platinum substrate from aqueous solutions of halides of antimony. Electrodes prepared by plating tend to behave in the same way as other massive electrodes but electroplating offers the advantage of enabling extremely pure samples of antimony to be prepared. The importance of obtaining electrodes of high purity was stressed by Roberts and Fenwick.[34] Powder electrodes consist of a mixture of finely divided antimony and antimony trioxide and appear to offer the performance which adheres most closely to the theoretical response. Stick electrodes tend to be favoured where small size or ruggedness is important.

The pretreatments recommended[2] by various authors appear to

offer little advantage apart from ensuring a clean oxidized surface. It has been reported that tarnished electrodes display greater reproducibility and accuracy. However, electrodes with thick oxide films tended to offer a more sluggish response and it is, therefore, advisable to recondition the electrode surface at regular intervals.

As a pH indicator electrode, the antimony electrode has the advantage of being rugged and inexpensive. Although it has a low resistance, it has a tendency to polarize and therefore, must be used in conjunction with an electronic voltmeter. It is susceptible to oxidizing and reducing agents and to complexing agents, particularly the anions of hydroxy acids (Chapter 7).

4.1.2 Bismuth Electrode[5]

Although originally regarded as a possible replacement for the antimony electrode, the bismuth electrode has proved to have certain disappointing characteristics. It has not been the subject of as many investigations as has the antimony electrode and in view of this fact is worthy of some further study. One possible advantage of the bismuth electrode over the antimony electrode lies in the fact that it is more stable and therefore less likely to adopt higher valency states.

Contradictory E° values put forward by various workers suggest that the potential is due to either the $Bi,Bi(OH)_3$ couple (0.4780 V at 25°C) or the Bi,Bi_2O_3 couple (0.3712 V at 25°C) although a monoxide has also been suggested as a possible oxide phase. It is by no means certain that this oxide exists although

it is possible that it may exist as a product of a mixture of Bi and Bi_2O_3.

A number of methods of electrode production have been quoted in the literature including electrodeposition on to graphite and platinum blanks, vacuum casting and the formation of amalgams. Surface oxidation may be achieved by exposure to air for several days or by dipping the bismuth into bismuth nitrate solution and heating gently.

Early examinations by Mehta and Jatka (cited in Ref. 5), showed that, over a limited pH range (5.0 to 7.4), the potential-pH slope was -60.11 mV/pH at 30°C (close to the theoretical value) with a temperature coefficient of -1.5 mV/°C. The electrode investigated was not treated or polished and unlike the antimony electrode, did not tarnish on storage under water. Dickinson and Rudge (cited in Ref. 5), observed a theoretical response, with rods of pure bismuth, over the pH range 5 to 8, but found that electrodes prepared by the electrodeposition of bismuth on platinum wire were unsatisfactory.

It has since been found that the bismuth electrode does not behave in a theoretical manner but shows pronounced salt effects in unbuffered solutions below pH 6. These effects are large and are dependent on the anion of the added salt. Potential displacement is always in the negative direction, non-instantaneous and there is an "overshoot". Even at higher pH values, the slope never attains the theoretical value. One explanation given in Ives and Janz's book[5] involves the hydrolysis of the bismuth ion to polymeric entities held together by oxygen bridges, the composition of this molecule being affected by an increase in pH .

Although it was originally thought that the electrode was insensitive both to stirring and to the presence of oxygen, it has since been found that it tends to behave as an oxygen electrode. Sammour and Moussa[35] working with deoxygenated buffer solutions obtained a potential - pH response line made up of four distinct sections, with breaks at pH 4, 8.5 and 11. These sections were assigned to the following potential determining reactions:

$$2Bi + 3H_2O \rightarrow Bi_2O_3 + 6H^+ + 6e \qquad (E^o_{obs} = 0.389\ V)\ (pH\ 11.5\ to\ 13.07) \qquad 4.1$$

$$Bi + 2H_2O \rightarrow BiO.OH + 3H^+ + 3e \qquad (E^o_{obs} = 0.366\ V)\ (pH\ 9.0\ to\ 10.5) \qquad 4.2$$

$$5Bi + 7H_2O \rightarrow 2BiO.OH + 3BiO + 12H^+ + 12e \qquad (E^o_{obs} = 0.335\ V)\ (pH\ 4.0\ to\ 8.0) \qquad 4.3$$

$$Bi + H_2O + Cl^- \rightarrow BiOCl + 2H^+ + 3e \quad (pH < 4.0) \qquad 4.4$$

Clearly the reaction shown in equation 4.4 ($E^o_{obs} = 0.160\ V$) will yield a potential - pH slope of 40 mV/pH. In oxygenated systems similar inflections were observed except that the breaks were less pronounced and the response line was displaced to more positive potentials.

It appears that the electrode is not prone to polarization and is much less sensitive to the presence of oxidizing and reducing agents than the antimony electrode.

4.1.3 Tungsten Electrode[5]

Early attempts at employing tungsten-tungsten oxide system as a pH indicator electrode met with limited success.[36,37,38] Each electrode was found to require its own calibration and potential - pH lines were high in slope and non-linear, e.g. Baylis[37] suggested that the catalytic activity of tungsten is desirable for electrode work and quoted a slope of 0.09 V/pH unit. Later workers[5] reported good potential - pH lines over the pH range 1 to 9.

Shatalov and Marshakov,[39] however, appear to have observed a flattening of the potential - pH response line from pH 6 to 10 under certain conditions and, in general, no single line was found to cover the entire pH range. Wakkad, Rizk and Ebaid[40] (1955) observed a pH - dependence of open circuit potentials, which was almost linear with changes of slope at certain pH values. The E^{o} values obtained in this particular investigation have been interpreted as not simple oxide potentials.[41]

It seems to be generally agreed that oxidative pretreatments serve no useful purpose, and may, in fact, be undesirable. No treatment at all, or boiling out with water appears to be sufficient to form an oxide film.

Anodizing in alkaline solution[41] results in the dissolution of tungsten to form a tungstate. However, if a certain current density is exceeded a kind of passivity results. This seems to be due to the formation of a film of the hexavalent oxide, which is redissolved on reducing the current. Britton and Dodd,[42] after anodizing a tungsten rod in sodium hydroxide solution (0.4 M)

by passing a current of 7.5 mA for 30 minutes, reported only a small variation in e.m.f. over the range pH 2 to 12, attributing this to passivation. (Unfortunately no mention is made of the potential employed in the preparative section of this work.) The oxide is not readily soluble in acid solution[41] and the metal forms a passivating oxide film on anodizing in acid solution.

From a thermodynamic point of view, tungsten is unsuitable as a metal-metal oxide electrode because it is not sufficiently noble in aqueous solutions of any pH, and in alkaline solutions tends to decompose water with the evolution of hydrogen. In acid solutions, however, the formation of the protective oxide film, mentioned above, prevents the corrosion of the metal. A protective layer such as this could be undesirable in a thermodynamically reversible electrode. Also, the stepwise formation of thin layers of oxides of increasing valency, observed under controlled anodic oxidation is undesirable, since a single potential determining reaction would be preferred on a reference or an indicator electrode.[40] Tungsten also has a tendency to reduce the higher oxide (WO_3). This would account for the negative 'creep' observed[40] in powder electrodes.

Despite these disadvantages, by virtue of its ruggedness alone, the tungsten electrode could be suitable for pH measurement (with adequate calibration) or for potentiometric end-point detection.

4.2 Experimental

4.2.1 Construction of Electrodes

The antimony electrodes were prepared, from metal of unknown specification, in the manner described by Short.[4] Molten antimony metal was drawn into pyrex glass capillary tubes using a pipette filler. The lower portion of each tube was heated with a bunsen flame, prior to dipping in the molten metal, in order to prevent premature solidifying of the metal. A number of stress marks were noticed in each metal core.

The samples containing the least number of flaws were cut perpendicularly across the tubes, in such a way that flat, smooth metal surfaces were obtained. All the electrodes were immediately transferred to distilled water and not subjected to any special pretreatments. The electrodes were then exposed to water for at least three days, before transferring to the test solution, in order to allow the metal surface sufficient time to oxidize.

Contact was made, within the electrode stem, by means of a drop of mercury. This enabled a thin shielded wire to be run down the entire length of the glass tube. In this way, extraneous electrical noise was reduced to a minimum. The wire shielding was insulated from the mercury using 'Lacomite' 'stopping-off' compound.

The electrodes prepared in this way measured 0.21 cm., 0.21 cm. and 0.12 cm. in diameter. These were recut whenever the response time became excessive and after exposure to noxious materials.

The bismuth electrodes used were prepared in a similar way,

but in this case, the molten metal (M.& B. Laboratory grade) was filtered through a grade 0 sinter (under an atmosphere of nitrogen), before casting in glass tubes. Oxidation was effected by exposing the electrode surfaces to air for three days. The finished electrodes were stored under water as in the case of antimony. The electrode diameter, in this case, was 0.19 cm.

Two tungsten electrodes were prepared from tungsten rod, (0.09 cm. diameter), sealed in glass tubes with approximately 1 cm. of metal projecting. Both electrodes were cleaned using fine emery paper and washed in distilled water.

The first electrode (A) was oxidized by exposing the metal surface to air for three days. The metal surface in the case of the second electrode, B, was oxidized by anodic polarization in the manner described by Britton and Dodd.[42] A potential was applied using a 6 V power source, (the potential used by Britton and Dodd was not specified), and a 440 ohm rheostat to control the current passing through the cell. The conditions of anodization were as follows:

N°	Current	Duration
B1	7.5 mA	30 mins.
B2	"	30 mins.*
B3	6 mA	15 mins.*

The electrodes marked * were cleaned by applying a reverse current for 10 seconds immediately prior to the polarization and the solutions used were made up with direct distilled water.

A platinum foil electrode sealed in a glass tube was used

as a cathode in each case, and the solutions were stirred at the slowest rate possible using a magnetic stirrer.

After oxidation, the electrodes were washed in distilled water and stored in potassium hydrogen phthalate buffer solution (Ch. 3) for several days.

Electrical contact was achieved in the same way as in the case of antimony electrodes.

4.2.2 Solutions

The composition of the 'U.B.' series of buffer solutions is dealt with in detail in Chapter 3. When used for the investigation of antimony and bismuth electrodes, unless otherwise indicated, 10 cm^3 of these solutions were diluted with 10 cm^3 of distilled water and then titrated with 0.04 M hydrochloric acid. In the case of tungsten, 20 cm^3 of universal buffer solution was titrated with HCl (0.04 M).

In the section dealing with the antimony electrode, reference is made to individual buffer solutions. These can be listed as follows: borax (0.01 M); potassium dihydrogen phosphate (0.0087 m) and disodium hydrogen phosphate (0.0304 m); potassium dihydrogen phosphate (0.025 m) and disodium hydrogen phosphate (0.025 m); acetic acid (0.1 M) and sodium acetate (0.1 M); potassium hydrogen phosphate (0.05 M) and potassium hydrogen tartrate (saturated at 21°C).

4.2.3 Procedure and Observations

A preliminary investigation was first carried out, in order to determine the general characteristics of the pH response. This was done by following the titration of perchloric acid with sodium hydroxide solution. 0.1 M perchloric acid (10 cm^3) was taken and diluted with distilled water (10 cm^3). Aliquots of sodium hydroxide (0.1 M) were run into the stirred solution. The pH of the solution was measured after 5 minutes, using the glass-calomel cell, and the potential of the antimony-calomel cell were taken 5 minutes after switching the antimony electrode into the circuit.

Obviously, this technique was not suitable around neutrality because of the rapid pH change in this region. Attempts were made to reduce the large carbon dioxide drifts, noticed in this region, by bubbling a steady stream of nitrogen through the solution. However, it was found that the oxygen response of the electrode was such that the rapid changes in oxygen partial pressure, brought about by the stream of nitrogen, caused sufficient 'noise' to make the potentials unmeasurable. The potential - pH slopes obtained were as follows:

pH range	slope (mV/pH)
0.75 to 1.5	0
1.5 to 3.2	-56
9.5 to 11.5	-60
11.75 to 12.5	-90

In order to determine the response of the antimony electrode

over the pH range 3 to 10, a series of individual amine buffer solutions was prepared. Tris was used to cover the pH range 7.2 to 10, a 0.1 M solution (20 cm^3) being taken, diluted with distilled water (20 cm^3) and then titrated with hydrochloric acid (0.1 M). A straight line with a slope of -56 mV/pH was obtained over the entire range.

This procedure, when repeated using Bis-tris as the amine component, yielded a curved plot with a best straight line of slope -52 mV/pH over the pH range 5.5 to 7.5. However, this plot was displaced to the negative side (-20 mV at pH 7).

The pH range 3 to 5.5 was covered by titrating a 0.1 M solution of tetramethyl ammonium hydroxide with succinic acid. It was found that a straight line plot with a slope of -59 mV/pH was obtained, displaced (at pH 5.5) by +15 mV with respect to the Bis-tris plot.

It was recognized that changing conditions would have an appreciable effect on the potentials measured, and so, the procedure was repeated with the entire apparatus inside an air thermostat. In this case, the experiments were carried out consecutively, allowing each solution to stand in the air thermostat for one hour before testing. It was found that all three solutions now gave potential - pH plots of similar slope. The Tris, Bis-tris, and tetramethylammonium hydroxide plots had slopes of about -55, -56, and -57 respectively. However, the Bis-tris plot was still displaced to the negative side by approximately -20 mV.

This discrepancy may be explained in two ways:

(a) The presence of the Bis-tris buffer in some way interferes

with the action of the electrodes.

(b) The removal of the electrode from the solution disturbs the equilibrium at the electrode surface.

In order to obtain more information about this effect, universal buffer solutions were prepared, thus eliminating the necessity to remove the electrodes from solution. It was found that the potential - pH plot obtained from U.B.1 (with Bis-tris) showed a slight displacement when compared to that obtained from U.B.2 (without Bis-tris); (see fig. 4.1). (Both solutions were diluted with an equal volume of water.)

This evidence was supplemented by carrying out an experiment with each universal buffer, to determine whether or not removal from solution has an effect on the electrode performance. In these experiments the electrodes were removed from the solution, (at pH 5.5 and 7.5), and allowed to stand in distilled water for 10 minutes before being returned to the universal buffer solution. These pH values were chosen because they were near to those at which the 'breaks' were reported in the literature. It was found that, at pH 7.5, there was no difference whatsoever, in either case, between the potentials observed before and after removal. At pH 5.5, though the potentials took longer to settle down, in both cases the difference in potential was insufficient to account for the discrepancies previously observed. Further experiments involved the plotting of a potential - pH curve from data obtained by the continuous titration of universal buffers using the Mettler titrimeter, automatic burette and recorder.

It is interesting to note that, even with solutions containing no Bis-tris, the slope in alkaline regions appears

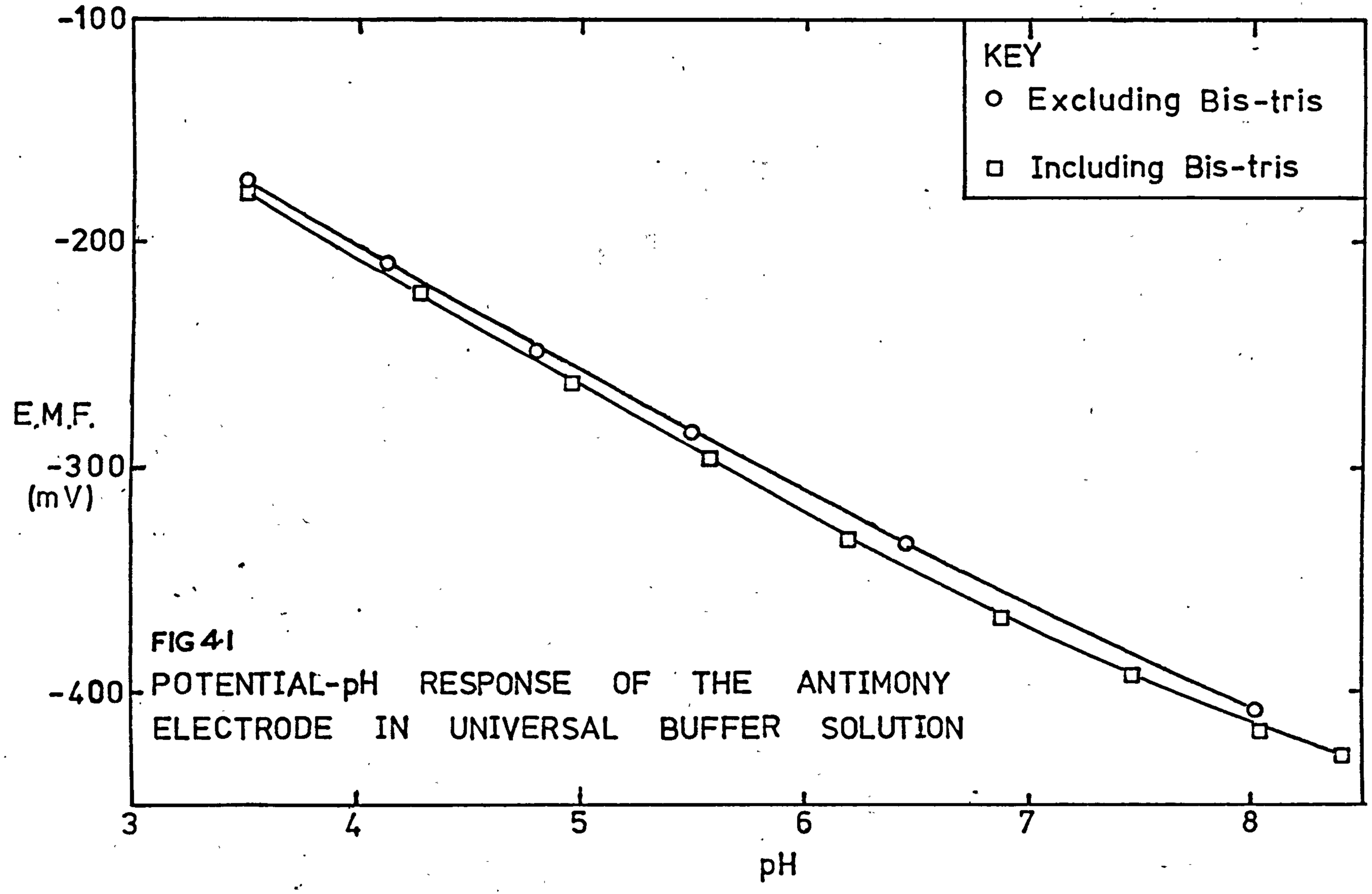


FIG 41
POTENTIAL-pH RESPONSE OF THE ANTIMONY ELECTRODE IN UNIVERSAL BUFFER SOLUTION

to be lower than in acid regions (e.g. -52 as opposed to -58). It was therefore necessary to observe the results obtained on changing the pH in the other direction, in order to find out whether or not the electrodes were affected by solution composition. This was done by carrying out a continuous titration with the Mettler titrimeter, burette and recorder, running in, at the slowest possible rate, sodium hydroxide (0.05 M) into 20 cm^3 of U.B.2 solution (acidified with 8 cm^3 of 0.1 M hydrochloric acid). In actual fact, it was found that the potential -pH line obtained from this experiment was almost superimposible on those obtained by the titration of U.B.2 with hydrochloric acid.

A number of results were obtained from individual buffers in the sequence shown in section 4.2.2. This method was found to be ineffective owing to the complexing action of the tartrate. In this solution, the response becomes erratic and a great deal of 'noise' is observed, together with a negative deflection of potential. The effect appears to be permanent. Phosphates, however, showed no such effect. From 4.6 to 7.4 a straight line with a slope of -57 to -58 mV/pH was obtained, but at high pH values a much lower slope was apparent. This was probably due to slow equilibration in the borax solution.

Finally, in order to verify that the effect of potassium chloride was responsible for the reported change of slope around pH 5, the response of the electrode in Clark and Lubs buffers was observed (compositions shown in Chapter 3). First, hydrochloric acid was used as an acidic component, then, this was replaced by perchloric acid in order to eliminate chloride ions from solution.

Steady potentials were recorded in these experiments giving results plotted in fig. 4.2. This shows clearly how the curve is displaced in the presence of chloride ions.

The antimony electrode, in general, showed a rapid response and normally appeared to give steady potentials within three minutes. Drifting, in the positive direction, was noticed around pH 5 in several cases; however, at no time was the rate of drift greater than 3 mV/hr.

It is interesting to note that the potentials obtained from the three electrodes in U.B.2 were in close agreement, but, in U.B.1 marked differences of up to 10 mV were observed.

Unlike those of antimony, bismuth electrode potentials display a marked tendency to drift, particularly in acid regions. Some positive drift is evident at values above pH 6 (when the electrode is examined in U.B.2), while under more acid conditions there is a negative drift to such an extent that the steady potentials show an apparently positive slope from pH 4.5 to pH 6. Below this value a negative slope is again observed.

As a result of these observations, it was decided to investigate the 'immediate' response of the electrode by continuous titrations of U.B.2. It was found that titrating the universal buffer ($20\ cm^3$) with HCl (0.04 M) gave a slope of -59 mV/pH over the range 7.5 to 8.5. However, at lower pH values, (3.5 to 7.5), a progressive flattening was observed. The titration of acidified U.B.2 with sodium hydroxide (see antimony), on the other hand, yielded an approximate straight line over the entire range (pH 2.5 to 8.5) with a slope of -52 mV/pH.

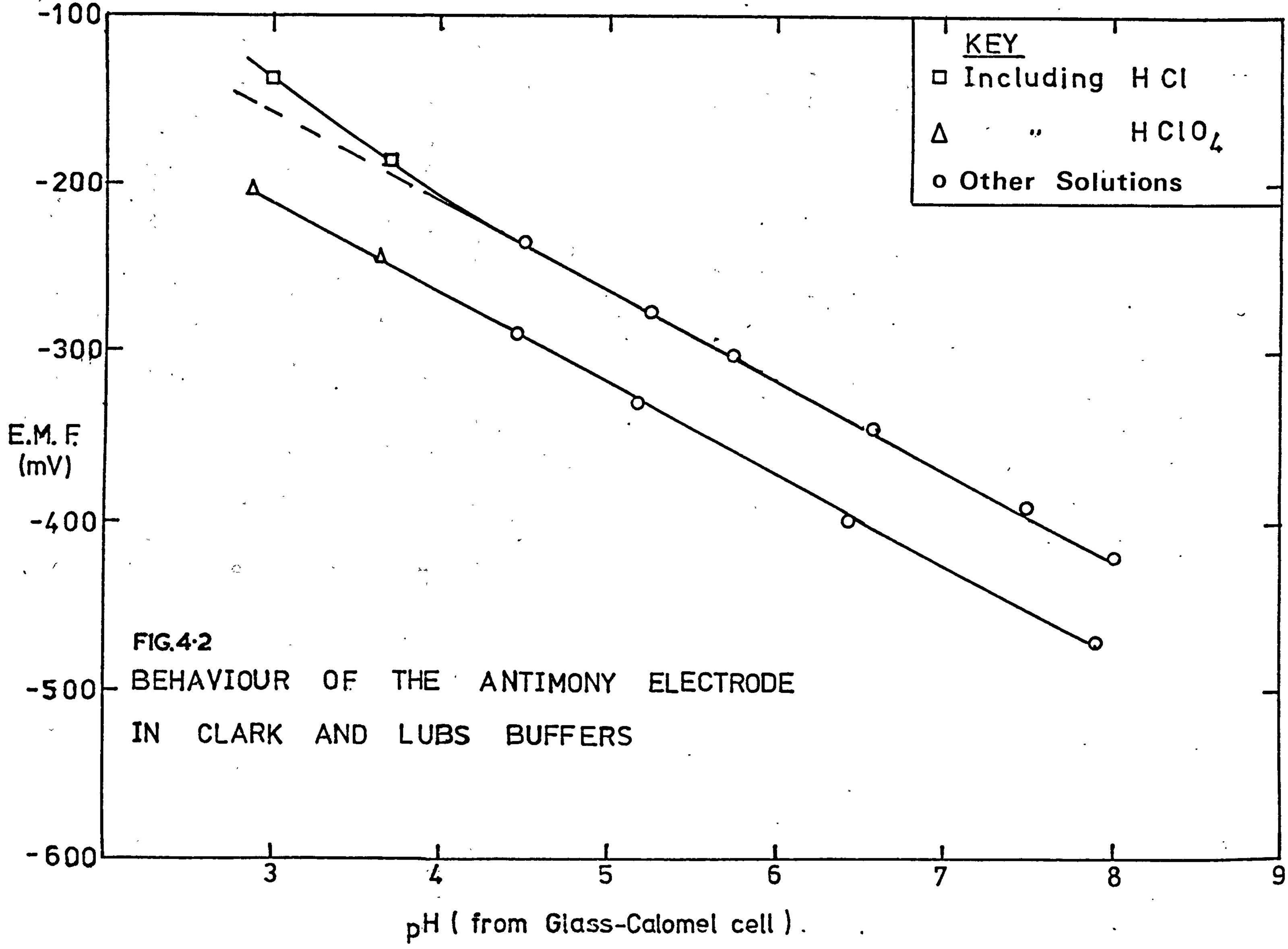


FIG.4·2

BEHAVIOUR OF THE ANTIMONY ELECTRODE IN CLARK AND LUBS BUFFERS

A tungsten electrode (air oxidized-A) was prepared in the manner described above. The pH response of the electrode was examined under stirred conditions in U.B.2 (20 cm^3) titrated with HCl (0.04 M) using the stepwise technique. A drift of potential in the positive direction was observed at all pH values, but was more pronounced under acid conditions, e.g. in the order of 4 mV/hr at pH 4.5. A best straight line of -31 mV/pH (± 10 mV) could be drawn through the points over the pH range 8.3 to 3.7, passing through pH 7 at -167 mV. The temperature of the solution was 19°C (± 1°C). Unless otherwise indicated, the temperatures of the solutions mentioned in this section should be taken as 20°C (± 1°C).

In this and the next chapter, unless otherwise indicated, drifts quoted signify those observed over the second hour that an electrode is exposed to a particular solution. Potential values at pH 7 are quoted in order that judgements can be made on the reproducibility of the electrode concerned.

Because of the observed drift in potential, it was decided to carry out a number of continuous titrations. An examination of the immediate response in U.B.2 titrated with HCl (0.04 M) yielded a good straight line over the range pH 6 to 2.3 with a slope of -32 mV/pH and if continued over the range 8.3 to 6 a best straight line of the same gradient (± 5 mV) was obtained, passing through pH7 at -205 mV. This deviation from the straight line, in this region, is not surprising since buffering is not complete from pH 6.2 to 7.9.

A continuous titration of 20 cm^3 of tetramethylammonium hydroxide solution (0.025 M) with succinic acid solution (0.05 M),

gave a gradient of -45 mV/pH (± 2 mV) over the buffered region (below pH 5) which could be projected through pH 7 at -235 mV. The difference between the gradients obtained from this and the previous experiment can be attributed to the drift noticed earlier. In this experiment, over the range pH 5.0 to 3.75 the pH is changed by approximately 0.05 pH $/cm^3$, while in the previous experiment, over the same range, the pH change was 0.3 pH units. As the titrant was introduced into the vessel at a constant rate, the rate of pH change is effectively six times more rapid. Therefore, in the tetramethylammonium hydroxide vs succinic acid experiment, the effects of the positive drift were considerably more noticeable.

In a third experiment, the pH was changed in the opposite direction, in order to examine any differences in response caused by variations in solution composition or experimental procedure. This was done by adding 8 cm^3 of HCl (0.1 M) to 20 cm^3 of U.B.2 solution and continuously titrating with sodium hydroxide solution (0.05 M). A good straight line of -36 mV/pH (± 2 mV) was obtained over the pH range 2.3 to 6 which became progressively flattened from pH 6 to 8.8. An overall straight line from this experiment was in the order of -35 mV/pH but with deviations of as much as ± 15 mV. The decrease in slope at higher pH values could be explained by a dilution effect, although an antimony electrode under similar conditions did not exhibit a similar response.

A number of tungsten electrodes was anodized as described above. It was found under a preliminary investigation that electrodes treated for 30 minutes in this way (B1 and B2) were

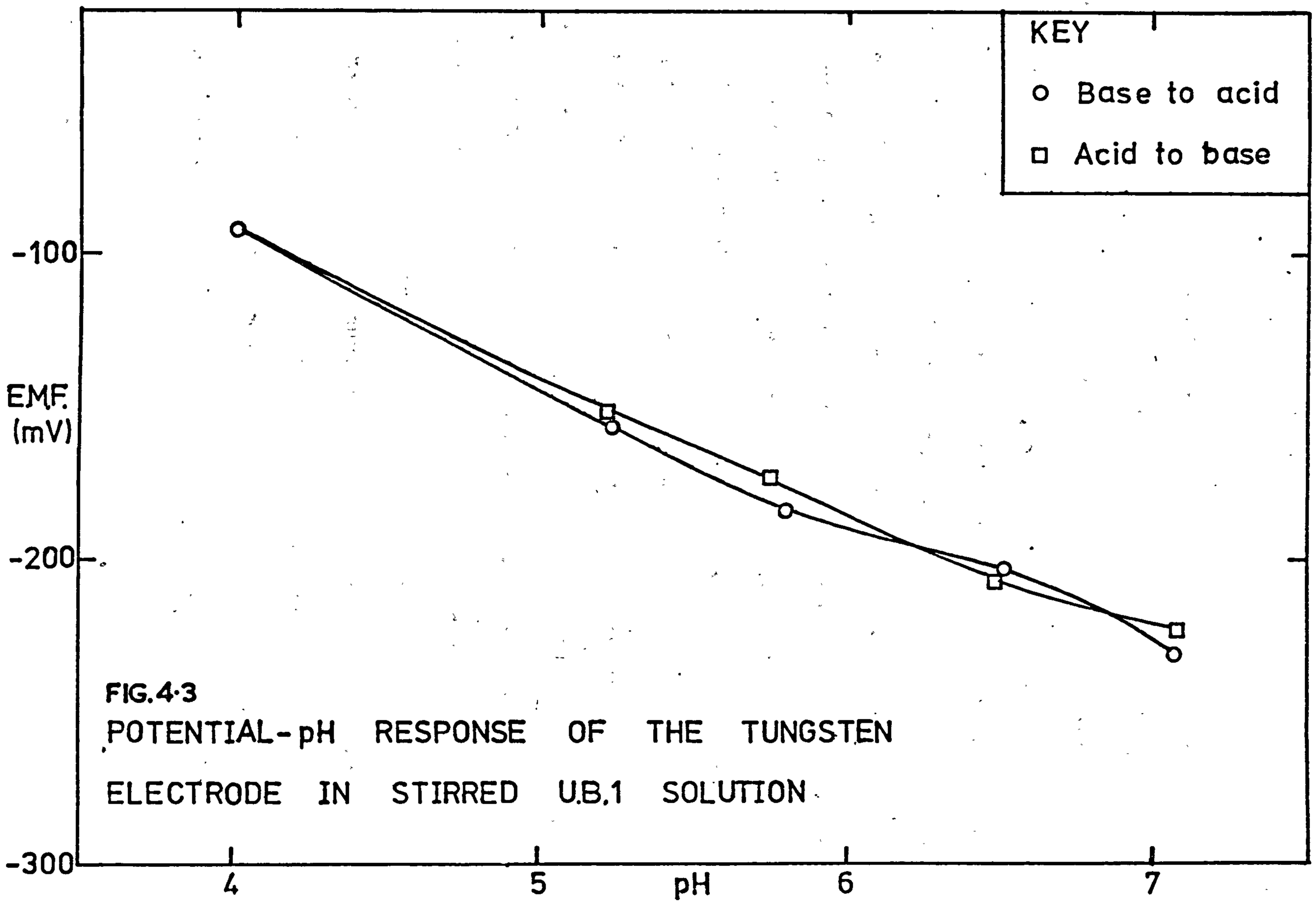


FIG.4·3
POTENTIAL-pH RESPONSE OF THE TUNGSTEN ELECTRODE IN STIRRED U.B.1 SOLUTION

extremely slow to respond between two buffer solutions at pH 4 and 8. The overall pH dependence displayed was in the order of -50 mV/pH.

The response of an electrode, anodized for 15 mins. (B3), was found to be much more rapid. When the e.m.f.s obtained from an unstirred solution of U.B.1 were plotted, a straight line graph of -39 mV/pH was obtained, which was displaced by about 10 mV in the positive direction under stirred conditions. This observation could possibly be accounted for by streaming potentials at the liquid junction of the calomel electrode. The plot obtained from the unstirred solution was found to pass through pH 7 at -235 mV. The electrode potential did show some tendency to drift in the positive direction but between pH 7 and 5 this was in the order of 1 mV/hr after the first 15 minutes.

A final experiment, again involving a stepwise titration of a stirred solution of U.B.1 (at 18°C) with HCl (0.04 M), was conducted followed by a subsequent reverse titration using tetramethylammonium hydroxide (0.1 M). The results of this experiment are shown in fig. 4.3. If a straight line is constructed through the curves obtained, a gradient of -44 mV/pH is obtained. This line is found to pass through pH 7 at a potential of -229 mV. The linear portions of the two curves have gradients of -52 mV/pH and -48 mV/pH respectively.

4.3 Conclusions

The response of the antimony electrode appears to be dependent, in some ways, on the composition of the solutions

in which it is placed. 0.1 M amine solutions yield slopes (over the pH range 3 to 8), of around -57 mV/pH. The universal buffer solutions (after dilution, 0.005 M with respect to each component) give potential –pH lines which tend to be curved, with lower slopes at higher pH values. On the other hand, Clark and Lubs buffers, in the absence of hydrochloric acid, give a good straight line plot with a slope around -54 mV/pH.

In most instances, the electrode response was extremely rapid (less than 3 mins.). However, at around pH 5 a certain amount of drifting was noticed. This would appear to be indicative of a change in E^{o}, but is not sufficiently rapid to affect appreciably the potential - pH line.

The presence of Bis-tris seems to have a temporary effect on the potentials observed. This effect seems to be dependent on the concentration of the buffer solution. In 0.1 M amine buffers, the negative displacement in potential was unmistakable. However, in universal buffers with a Bis-tris concentration of 0.005 M, the observed displacement was small enough to be explained by changes in conditions. It is known that certain neutral salts, when present in solutions in large enough quantities, have the effect of displacing oxygen from solution.[5] This causes a negative displacement in potential. It is possible that Bis-tris has the same effect or in some other way affects the concentration of 'available' oxygen.

Tartrates show a large permanent effect on the electrodes. If phosphates cause changes in the electrode surface, as suggested by Bishop and Short,[30] then the effect would not appear to alter the nature of the potential - pH curve. Complications due to the

variation of phosphate concentrations are also reported in connection with electrode calibration by Green and Gielsisch.[28] Potassium chloride, on the other hand, appears to displace the curve to the positive side.

The individual reproducibility of electrodes prepared from the same sample of metal appears to be good, but any discrepancies tend to be aggravated by the presence of Bis-tris.

The antimony-antimonous oxide electrode is not worth considering as a reference electrode because of the high pH response and the large number of extraneous effects. The use of the antimony electrode as an indicator electrode is well known (section 4.1), however, in view of the various interferences, it is desirable that a serviceable alternative should be found.

Bismuth would appear to be useless, either as a reference or an indicator electrode, because of the considerable drift in potential exhibited at most pH values. The 'positive' slope observed would appear to be due to a large, gradual change in E^{o} around pH 4. This could be due to a changing dominance between more than one electrode reaction. This is consistent with the observation reported in section 4.1 that a change in dominance from reaction 4.3 to reaction 4.4 takes place at around pH 4. The change in E^{o} of -175 mV could easily account for this 'positive slope'. Providing the solution pH is changed rapidly, this electrode could be suitable for titrimetry.

Tungsten electrodes, oxidized in air, have often been used as pH electrodes. This investigation, however, would seem to indicate that the electrode is, in fact, unsuitable for this purpose. Slopes in the order of 31 to 32 mV/pH would normally

be considered too low for an indicator electrode and drifts of around 4 mV/hr may be considered excessive. The various results quoted in the previous section imply a very slow response. This would again be undesirable for these purposes.

Tungsten electrodes prepared by 'harsh' anodic polarization were found to be partially passivated but even so had comparatively high pH responses. The general responses were, not surprisingly, even slower than those observed with the air oxidized electrodes, but were more rapid when anodization was limited to 15 mins. rather than 30 mins.

The electrodes prepared were quite unsuitable either as indicator or reference electrodes. It would, however, be interesting to make an electrode by anodizing it under milder conditions using the more sophisticated equipment employed in Chapter 6.

Chapter 5

NOBLE METAL ELECTRODES

5.1 Introduction

Noble metals like other metals are not inert to electrolytes containing dissolved oxygen. When a certain potential with respect to the S.C.E. (see later sections) is exceeded, a chemically bound oxygen layer is formed on the metal surface.[43]

Since this was realized, a number of investigations into anodic oxygen film formation and cathodic dissolution have been carried out. A great deal of the research into the electrochemical behaviour of noble metals has been directed towards finding out the nature of the electrode phenomena responsible for the irreversibility and poor reproducibility of the oxygen electrode on noble metals. However, a number of fundamental questions concerning these phenomena, the mechanisms of anodic and cathodic processes, as well as the nature of the film are still unanswered.

A detailed study of the various phenomena mentioned above would be irrelevant to this investigation. If, however, the pH response of noble metal-noble metal oxide electrodes is to be examined, a brief survey of the literature available must first be undertaken in order to determine an appropriate method of obtaining a suitable oxide film. It is also desirable that any problems inherent in its production and use should be known. The

introduction to this chapter below includes such a survey.

The use of noble metals as pH or reference electrodes is not widespread. In addition to the work of Every et al.,[44,45] (discussed in a later section of the chapter), the use of noble metal-noble metal oxide electrodes prepared in a similar manner has been reported by Dobson et al.[46] who find that in air equilibrated solutions, platinum, iridium and rhodium electrodes show a less than ideal pH response. If this is the case then it is possible that electrodes of this kind may be found useful for reference purposes.

These findings contrast with the titrimetric work of Malmstadt and Fett[6] which shows for rhodium and platinum-rhodium mixtures a potential - pH response roughly comparable to that of antimony and glass electrodes. This difference could be due to the presence of thick oxide films in the former case or perhaps to a 'time effect' (see later). Palladium and iridium have also been reported to be suitable for pH measurement in G.B. Patents 1,348,837[47] and 567,722[48] respectively. The potential - pH slope in the case of palladium was in the order of 59 mV/pH and in the case of iridium 60 mV/pH was quoted. If these findings are applicable for other noble metal systems, then these materials could provide a suitable basis for useful pH indicator electrodes.

In this chapter the pH behaviour of platinum, rhodium and gold systems are examined separately.

5.1.1 Platinum-Platinum Oxide Electrodes[49,50]

In oxygen-containing solutions, platinum displays an open circuit potential of about +0.9 V vs hydrogen. A reversible oxygen electrode would have a potential of 1.23 V. The failure to take up the oxygen potential has been interpreted in a number of ways.

The discrepancy was first explained by the presence of oxides, the rest potential being determined by the oxide/oxygen couple in place of the metal/oxygen couple. However, on examining the open-circuit potential of preanodized platinum electrodes as a function of time, plateaux not corresponding to potentials for any known oxide were obtained. This was first attributed to the presence of higher oxides and to varying ratios of an ill-defined oxide, PtO_x.[50]

The oxide theory was eventually shown to be inappropriate by Bain, who compared the behaviour of platinum to that of other similar metals. He discounted the oxide theory since the rest potential of each metal reached a common value with time. If the potential were only determined by a metal/metal oxide reaction or by a metal oxide in equilibrium with oxygen, the rest potentials would be quite different.[50]

Another theory put forward, hinged on the rest potential being dependent on the concentration of peroxide in solution. This theory accounted for the detected presence of H_2O_2 in solution and for observed stirring effects. However, later work showed peroxides to be absent under open circuit conditions, and the dependence of potential on stirring rate was explained in

other ways.[50]

A third explanation involves a mixed potential mechanism, the electrode system being a polyelectrode. According to this theory, the oxide film has cracks in it or is permeable to the solution. In this way, a local cell is set up, oxygen reduction taking place on the surface of the film, and platinum oxide being formed on the metal surface. The actual details of the processes involved are debatable, but such a system could be used to explain the response of the electrode to dissolved oxygen and other observed phenomena.[50]

The Oxides of Platinum[50]

Although oxides, apparently, do not play an important part in the processes described above, a number of oxides of platinum are, in fact, obtainable. It would appear that the only stable oxide is PtO_2, which can be chemically prepared by boiling $PtCl_4$ with sodium hydroxide and subsequently adding acetic acid. This process yields white $PtO_2 \cdot 3H_2O$. The molecules of water can be removed in a stepwise manner, eventually yielding black, anhydrous PtO_2. A yellow tetrahydrate has also been reported.

Another oxide PtO ($Pt(OH)_2$ when hydrated) may be prepared by the action of hot alkali on $PtCl_2$ or K_2PtCl_4. This oxide, apparently, has to be kept in a carbon dioxide atmosphere in order to avoid atmospheric oxidation to PtO_2. The compound is highly unstable, and disproportionates to Pt and PtO_2

$$2\ PtO \rightarrow Pt + PtO_2 \qquad 5.1$$

A dark brown sesquioxide, Pt_2O_3, has been reported, as has the reddish-brown PtO_3. The former seems to have properties lying between PtO and PtO_2 and the latter is extremely unstable. Pt_3O_4, which has been reported by some authors, is likely to be merely a mixture of PtO and PtO_2.

It appears that the application of A.C. or D.C. to a platinum electrode in sulphuric acid results in the production of a visible film of PtO_2.[49] A method of preparing a mixture of PtO and PtO_2 on a platinum surface has been described by Every and others.[44,45,51,52] This method, employing fused oxidizing agents, is dealt with in more detail later in this chapter.

The Nature of Oxygen Films on Platinum[50]

The nature of surface films on platinum is still, it appears, the subject of some debate. It is now established that, in an oxygen saturated medium, platinum surfaces will adsorb oxygen in the form of an electronically conducting film approximately a monolayer thick. When the metal is polarized anodically, oxygen adsorption begins at about 0.8 V. Hoare[50] suggests that this film does not grow beyond a thickness of one monolayer, even on prolonged anodization. Oxygen evolution begins after the formation of this monolayer.

The exact form of this adsorbed oxygen is not known for certain. It has been suggested by some workers that, below 1 V., PtO is formed while at potentials above 1 V a mixture of PtO and PtO_2 is produced. This was determined by Anson and

Lingane (cited in ref. 50), to be in the ratio of 6:1, the proportions being constant under more strongly oxidizing conditions, even though more oxide was formed. The balance would be expected to tip in favour of PtO_2. This examination was carried out by spectrophotometric analysis for $PtCl_4^{2+}$ and $PtCl_6^{2-}$ after chemically stripping part of the 'oxide' film.

This technique has been criticized by Breiter and Weininger (quoted in ref. 50), who concluded that these results could be explained by a mixed potential mechanism such that the platinum in solution comes from the metal and not the oxide, accounting for the fixed ratio observed. This criticism which is dealt with in detail in Hoare's book[50] can be applied to the work of Every and Grimsley[51] (see later).

Another possibility is that oxygen could be adsorbed on a platinum surface as atoms, by a dissociative adsorption process. It has been reported that one atom of adsorbed oxygen is associated with one atom of platinum. It is, however, undecided whether the oxygen is present in the molecular or atomic form.

Yet another suggestion is that, after a monolayer of oxygen has become adsorbed on the platinum surface, any further oxygen is dissolved in the metal as a Pt-O alloy (dermisorbed oxygen) to the extent of 3 or 4 layers of absorbed oxygen. A summary of the evidence for this theory is given in "The Electrochemistry of Oxygen" by Hoare[50] but it would be inappropriate to go into detail here.

The behaviour of open circuit potentials with respect to stirring has been briefly referred to earlier, however, no specific details were obtainable during the compilation of this

literature survey.

The response of the platinum electrode with respect to dissolved oxygen is, again, dealt with in detail by Hoare[50] who quotes, amongst others, values obtained by Bockris. In this investigation it was found that, at low oxygen pressures, a variation of about 60 mV/log P_{O_2} was obtained which decreased to a value of 15 mV/log P_{O_2} above 0.2 atm.

It has been demonstrated that the electrode potential is a function of the degree of coverage of the metal surface, therefore, differences in observed values of the potential may be explained by changes in the oxygen coverage of the electrode. This can be expected to depend on any pretreatments received by the electrode involved. The observation that oxygen coverage of a platinum surface is related to the square root of the oxygen partial pressures has been used as evidence for dissociative adsorption.

Hoare quotes the rest potential as changing by approximately 60 mV per pH , but acknowledges that this is difficult to explain in terms of a mixed potential system, since the potential should depend solely on the number of oxygen dipoles absorbed on the surface.

The fact that the nature of the films on platinum surfaces is, even today, not settled, is illustrated by a recent study by Dickinson, Povey and Sherwood[53] using X-ray photoelectron spectroscopy (X.P.S.). This work shows a linear growth of oxide with potential, where PtO is the predominant species, but not at higher potentials where PtO_2 is the principal oxide formed. Chemisorbed oxygen is also shown to be present under the conditions

of the investigation. The work of Parsons and co-workers, quoted in this thesis, apparently suggests that PtO_2 is formed on top of a PtO layer.

5.1.2 Rhodium-Rhodium Oxide Electrodes[54]

It appears that the only stable oxide of rhodium is Rh_2O_3 and that compounds with a higher oxygen content than this cannot exist. This highly insoluble, grey compound can be produced by heating rhodium above 600°C in air or oxygen but may decompose on heating above 1,150°C. Reports of RhO and Rh_2O can be accounted for by mixtures of Rh_2O_3 and Rh. The dioxide, RhO_2, can be made only in the hydrated form.

Charging curves from nitrogen-stirred solutions, both acid and alkaline, indicate that a layer of adsorbed oxygen is formed before oxygen is evolved. It seems that these films are good electronic conductors and so do not grow to much more than one layer.

Rest potential studies indicate that more tightly bound films are obtained with anodic polarization. It appears that, although the presence of Rh_2O_3 is likely, anodization enables oxygen to become dissolved in the outer layers of the metal surface to form a Rh-O alloy, $Rh(O)_x$ in the same way as platinum.

Potential sweep curves show that oxygen begins to adsorb at less noble potentials than on platinum. Apparently, the oxygen absorbed during anodic sweeps is so strongly held, particularly in alkaline solutions, that the oxygen reaction

region overlaps the H^+ ion reduction region. A skin of $Rh(O)_x$ is likely to be reduced only with great difficulty. Potential sweep studies, in fact, appear to bear out this assertion.

In an oxygen-saturated, peroxide-free solution of sulphuric acid (1M), a rest potential of 0.88 V is observed. This rest potential has been found to be dependent on pH (60 mV/pH) but is independent of P_{O_2}. Again, this response is likely to be a mixed potential comprising the O_2/H_2O reaction and a $Rh/Rh(O)_x$ reaction. The latter reaction is likely to proceed according to the equation:

$$Rh(O)_x + 2xH^+ + 2xe \rightarrow Rh + xH_2O \qquad 5.2$$

and would have to be potential determining in order for the rest potential to be P_{O_2} invariant. This dermisorbed oxygen can, apparently, also be produced by heating the metal in air.

Hoare[54] concludes that oxygen is bound to rhodium in at least two ways: strongly by anodization and weakly by the adsorption of oxygen dissolved in solution. Under open-circuit conditions, an oxide-free rhodium electrode (pretreated with hydrogen), in contact with an oxygen saturatedacid solution, adsorbs oxygen as a mono-atomic layer. Under these conditions, a steady potential of 0.93 V has been observed, within about 24 hrs., which is dependent on the P_{O_2} to the extent of 15 mV/log P_{O_2} and on the pH to the extent of 60 mV/pH. A polyelectrode explanation has, again, been put forward, the potential being due to the O_2/H_2O reaction (equation 6.19), which would have to

be potential determining in order to account for the observed dependence on P_{O_2}, and the Rh/Rh-O reaction:

$$Rh\text{-}O + 2H^+ + 2e \longrightarrow Rh + H_2O \qquad E^\circ \quad 0.81\ V \qquad 5.3$$

It has also been concluded that this Rh-O film is no more tightly bound than in the case of platinum.

Since the film of adsorbed oxygen is electronically conducting and complete, the metal surface is truly inert to oxygen and so the reversible oxygen potential (1.23 V) is obtainable using electrodes treated with concentrated nitric acid.

5.1.3 Gold-Gold Oxide Electrodes[55]

It appears that, although other oxides of gold may be formed, only Au_2O_3 or $Au(OH)_3$ is stable.[55,56] The highly unstable brown oxide, AuO, may exist, but the black precipitate of Au_2O, reported by some investigators, has been proved to be a mixture of the reddish brown Au_2O_3 and colloidal gold.

Of the workers employing anodic constant-current changing curves, only El Wakkad and El Din,[57] (working with gold plated platinum electrodes at low current densities) have reported the presence of Au_2O and AuO. The consensus is, however, that only one oxide is formed electrochemically, formation beginning at 1.35 V, and that gold does not dissolve oxygen in the same way as platinum or rhodium. Potential sweeps also show the presence of Au_2O_3 only.

On anodization, Au_2O_3 is formed as a flaky, poorly

adherent film, which continues to grow with time. This observation suggests that gold oxide films are better ionic than electronic conductors. Dickinson, Povey and Sherwood, carrying out X.P.S. studies, observe the formation of Au_2O_3 only, and an approximately linear increase of thickness with potential. Below 1 A/cm^2, gold, apparently, does not build up visible oxide films, a monolayer only of Au_2O_3 being formed.[55]

An E^o value for the Au/Au_2O_3 system has been found using a gold wire dipped in a slurry of fine Au crystals and Au_2O_3 in a sulphuric acid solution. The equation for the reaction would be:

$$Au_2O_3 + 6H^+ + 6e \rightarrow 2Au + 3H_2O \qquad E^o = 1.36\ V \qquad 5.4$$

An unoxidized gold electrode, (treated with hydrogen), in an oxygen saturated solution has a rest potential of between 0.7 and 0.8 V. This drifts towards a steady value of 0,98 V. An electrode previously polarized above 1.4 V, on the other hand, drifts through 1.36 V to lower potential.

There appears to be no doubt that the rest potential of 1.36 V, observed in acid solutions, is due to the Au/Au_2O_3 reaction, (a true metal-metal oxide system). In such a system, the electrode potential is independent of P_{O_2} and varies by 60 mV per pH .

Gold oxide is unstable in acid solutions[55] and disappears with time, the appearance changing from reddish-brown to black. This is accompanied by a decrease in potential to about 0.98 V. Most of the Au_2O_3 is reduced to Au black but some gold may go

into solution as a complex. The oxide is, apparently, more soluble in alkaline than in acidic solutions, the solutions turning yellowish when gold is anodically polarized. The rest potential in potassium hydroxide solution is quoted in Hoare's book as about 1.1 V, accounting for the deviation from 1.36 by the large amount of gold present in solution.

The only controversy appears to relate to whether or not oxygen is adsorbed below a potential of 1.3 V. It appears that the steady rest potential of 0.98 V indicates that gold adsorbs oxygen from oxygen saturated solutions, if not in the dry state.

The rest potential at 0.98 V seems to be best explained by mixed potentials. In this case, the local cell set up on the gold surface would consist of the O_2/H_2O and Au/AuO reactions, the rest potential being controlled by the latter:

$$Au\text{-}O + 2H^+ + 2e \rightarrow Au + H_2O \qquad 5.5$$

This would account for the fact that the potential of such an electrode has been observed not to change with variations in the P_{O_2} but is seen to be pH responsive (60 mV per pH).

Hoare attributes variations in the rest potential with time to changes in the activity of the Au-O layer with the amount of oxygen adsorbed on the surface.

The reversible oxygen potential is not observed on gold. This is explained in Hoare's book by the fact that a complete, electronically conducting film can never be formed and therefore the gold surface is never truly inert to oxygen.

5.1.4 The Formation of Thick Oxide Films on Noble Metals

As can be seen from the previous sections of this chapter, the bulk of the work carried out on noble metal oxides to date, mainly relates to the electrochemical preparation and investigation of thin oxide films, one or two atomic layers thick. Laitinen and Enke[51] concluded that oxide films on platinum are electron conducting rather than ion conducting and so do not grow to be more than one or two atomic layers thick. This is, however, by no means certain (see earlier).

Although thin films are probably desirable from the point of view of rapid equilibration and response, it can be seen in Chapter 1 that a substantial oxide layer is necessary to ensure stable potentials controlled by a single electrode process. For this reason the methods chosen for the oxidation of massive noble metal electrodes in this investigation were those described by Every and co-workers.[44,45,51,52]

Every et al.[44,45,51,52] who were primarily concerned with the production of reference electrodes for use in anodic corrosion control, have, however, put forward methods of forming thick oxide films on noble metals by chemical means. These oxides were analysed by X-ray or electron diffraction[52] and direct methods of analysis.[51]

A Pt-PtO surface was prepared by placing a platinum black electrode in an oxygen atmosphere at temperatures in excess of 465°C for several hours.[45,52] The films obtained, by this method, were described as black below 500°C and grey above 500°C.[52]

PtO/PtO_2 surface films were claimed to be obtained by

dipping a platinum electrode in fused potassium nitrate at $400^{o}C$.[44,45,51] It seems that the oxide film, prepared in this way, does not increase in thickness after about an hour. The appearance of electrodes treated thus, was described as changing from shiny to lustreless. No colour was apparent, even after 20 hours.[51] A $PtO:PtO_2$ ratio in the region of 7:1 was determined by spectrophotometric analysis of chemically stripped films.[45,51] The techniques employed in this form of analysis have been criticized by other workers (set out in full in ref. 50) (see earlier section of this chapter).

Every and associates also carried out a number of experiments involving the electrolysis of molten salts, namely potassium nitrate and potassium chlorate.[44,51] Figures quoted for potassium nitrate[51] show that a coherent oxide film is obtained much more rapidly by this method and that the amount of PtO_2 produced on the electrode is almost doubled. The thickness of the oxide film (12 to 157 atomic layers), seems to depend upon the method employed rather than the reaction time.[44] In time, films prepared by this method tend to stabilize at 60 atomic layers while films prepared without electrolysis tend to be no thicker than 15 atomic layers.[51] Films prepared using electrolysis tended to be extremely adherent, particularly those prepared at low current densities. Appearance tended to vary from light to dark brown, depending on the current density employed.[51] Since an extremely thick oxide is likely to cause slow electrode responses, the use of electrolysis is likely to be of little value in the present investigation.

A similar method was employed for the oxidation of rhodium to rhodium oxide, the metal being exposed to fused potassium nitrate

at 400°C without electrolysis, for periods in excess of 12 hours.[44,45,52] The formula of the oxide was identified as Rh_2O_3 by X-ray diffraction.[44.52] The $Rh-Rh_2O_3$ films prepared in this way were described as having a dull appearance.[52]

The exact temperature employed for the oxidation of metals, by the general method of using molten oxidizing salts, is apparently not critical in the formation of the oxide.

The oxidation of gold was carried out by Every and associates, by making the metal the anode in sulphuric acid 4.5M.[45] The sulphuric acid concentration used appears to have been chosen on the basis of galvanostatic work carried out by El Wakkad and El Din.[57] The reason for the choice of this concentration is unclear, as the work, quoted above, appears to imply that very little oxide film (if any) is deposited under these conditions. It is possible that this was done in order to limit the number of possible oxide species, since work also indicates the presence of species other than Au_2O_3 and, in fact, the oxide produced above is claimed to be Au_2O.[45]

5.1.5 The Properties of Noble Metal/Noble Metal Oxide Electrodes Prepared in the Work Described Above

Every and Banks[45] claim that under strongly acidic conditions $Pt-PtO : PtO_2$, $Au-Au_2O$, and $Rh-Rh_2O_3$ half cells give more reproducible e.m.f.s than the saturated calomel electrode.

These three electrodes are claimed to show almost identical e.m.f. behaviour and values in different acid[44,45] conditions,

the e.m.f. values being reproducible to ± 20 mV. All three systems apparently give e.m.f. values essentially independent of sulphuric acid concentration below 96% and above 100% concentration. Pt-PtO electrodes seem to be regarded as inferior to those quoted above, giving e.m.f. values reproducible to ± 30 mV.

According to Every and Banks[45] all these noble metal-noble metal oxide electrodes exhibit a similar temperature dependence which is linear, and in the order of 1 to 2 mV/°C. The temperature stability of platinum-platinum oxide electrodes apparently varies with the electrolyte used.[44]

Au_2O_3 electrodes are claimed to show steady e.m.f.s after 15 minutes in oleum , these values being maintained for about 24 hours.

It should be emphasized that although apparently favourable claims are made in references,[44,45,51,52] as listed above, these do relate to extreme conditions of acidity. It is possible that, under the more moderate conditions of this investigation, completely different electrode characteristics may become apparent. Furthermore, at the acid concentrations quoted above, the pH change corresponding to a comparatively large change in concentration is likely to be minute, thus accounting, at least in part, for the independence of e.m.f. on acid concentration. The characteristic change in e.m.f. from 96% to 100% concentration is presumably due to a change from aqueous to effectively non-aqueous conditions.

5.2 Experimental Section

5.2.1 Construction of Electrodes

The methods of oxidation employed were based on those suggested by Every and others.[44,45,51,21]

The platinum-platinum-oxide electrodes were prepared by immersing a piece of platinum foil (welded to platinum wire which was in turn sealed into glass), in molten potassium nitrate in the manner described by Every and others[44,45,51] (see Introduction).

Prior to oxidation, the foil was polished with fine emery paper (type 2/0), boiled in aqua regia for 1 minute and washed in distilled water. It was found necessary to heat up the nitrate with the metal under the surface of the cold salts in order to avoid cracking the glass tube. This situation was further complicated by the need to immerse the tip of the glass tube, as well as the metal, under the surface of the oxidizing medium in order to ensure complete oxidation of the platinum surface.

The actual oxidation was carried out by heating fused potassium nitrate (G.P.R.) in a silica crucible for 1 hour. In the absence of specialized equipment, capable of measuring high temperatures, a temperature of 400 to 500°C was approximated by using a bunsen burner at full heat. After 1 hour, the fused salt was allowed to cool and dissolved in distilled water. The resultant electrode was washed and stored in distilled water prior to testing.

The principal method employed for the oxidation of rhodium was almost identical to that used for the platinum electrodes,

except that, in this case, the electrode was not polished with emery paper. Cleaning was achieved by exposing the electrode 'blank' to hot aqua regia for just long enough to clean but not etch the metal surface. In this case, the electrodes were oxidized for 1 hour or a half hour. It was decided not to heat the electrodes for 12 hours as suggested by Every[44,45,52] (see introduction), as the heavy oxide coatings which would probably be formed might increase the response time of the electrodes.

This method was modified slightly for some tests, in that a preoxidized wire (1 hr.), already welded to a platinum wire of similar dimensions, was sealed in epoxy resin (Bostik) in such a way that the metal-metal joint was covered. The surface of the resin was built up so that a smooth, convex surface would be presented to the solution. Electrical connections were made using mercury in the usual way.

Another technique employed to oxidize metallic rhodium involved anodic polarization in sulphuric acid (2.3 M) (reference: The Electrochemistry of Oxygen, p. 56).[55] The potential of a rhodium wire electrode, sealed into glass, was maintained at 1.044 V with respect to a saturated calomel electrode by means of a potentiostat and a three electrode system. This comprised the rhodium working electrode, a Radiometer saturated calomel electrode, and a platinum counter electrode. The working and reference electrodes were held in the same compartment, as near as possible to each other (approximately 2 cms) in order to keep the ohmic drop as low as possible. In addition, a second saturated potassium chloride salt bridge (No. 4 Sinter glass frit) was

incorporated into the S.C.E. in order to lessen the danger of contamination of the calomel electrode with sulphate ions.

The anodization was continued for 17 minutes, after which the electrode was removed from solution the moment before switching off the potentiostat. The oxidized electrode was then washed with distilled water and stored in a phosphate buffer at pH 7.

The gold electrodes tested in this investigation were constructed from lengths of gold wire (0.8 cm diam.), sealed in glass tubing with 1.6 cm projecting. Since gold forms an amalgam with mercury, electrical contact was made by welding the enclosed end of the gold wire to a length of copper wire passing down the entire length of the glass tube. The copper wire was then soldered to a length of screened coaxial cable. Before anodizing, each electrode was polished with fine emery paper (2/0), cleaned with aqua regia and washed with distilled water before storing in a phosphate buffer.

The first gold electrode tested (A), was prepared in the 4.5 M sulphuric acid solution suggested by Every and Banks.[45] The conditions of anodization chosen were such as to produce a layer of colloidal gold i.e. a potential of approximately 2.33 V was applied for one hour with a steady current of 14.5 mA. This was carried out using the simple apparatus described for tungsten.

It was decided that sulphuric acid (0.5 M) would be a more appropriate medium for oxidation than that suggested by Every, and that the more sophisticated apparatus described for rhodium should be used. Since oxidation commences at around 1.1 V with respect to the S.C.E. and colloidal gold is formed above 1.8 V,[58] a

potential of 1.5 V was chosen for most of the work on the gold-electrode.

Electrode B was polarized at this potential for 15 mins., after first etching in aqua regia. Electrode C was prepared in a similar fashion, but, in this case, the electrode blank was not etched, exposing the wire to aqua regia for only 2 secs.

A fourth electrode (D) was anodically polarized at a potential of 1.2 V for 15 mins., in order to obtain a thinner film.

5.2.2 Solutions

The preparation of the solutions used in this chapter have already been described (Chapter 3). The mixtures U.B.1, U.B.2 and U.B.2 (made alkaline with T.M.A.H.) were made up as described, 20 cm^3 being titrated with hydrochloric acid (0.04 M).

In addition various individual test solutions were employed (referred to in Chapter 2) as follows:

Solution	Concentration	Approximate pH
Tetramethylammonium hydroxide	0.1 M	13
Ethanolamine (Titrated to pH 9.9 with HCl (0.04 M))	0.1 M	9.9
Potassium dihydrogen phosphate	0.025 m	6.86
Disodium hydrogen phosphate	0.025 m	
Potassium hydrogen phthalate	0.05 m	4
Hydrochloric acid	0.1 M	1

5.2.3 Platinum Electrodes

When electrodes prepared in the manner described in section 5.2.1 were subjected to stepwise titrations using stirred U.B.1 solutions and the electrode potentials allowed to stabilize in the usual way, a dip in the potential - pH line was observed between pH 6 and 7 (fig. 5.1). The extent of the dip was dependent on the time allowed for equilibration. The positioning of this dip on the pH scale was dependent on the composition of the solution involved, displacements being noticed when U.B.1 was replaced with U.B.3 and when the direction of titration was reversed.

In order to determine whether this phenomenon was related to the presence of Bis-tris (as in the case of the antimony electrode), an experiment was carried out involving the addition of weights of Bis-tris to a solution of Bis-tris (0.0023 M). The pH of this solution was then titrated to 6.50 and the potentials of the platinum electrode noted. It was found that, over concentrations from 0.0023 M to 0.016 M, the potential measured after 2 hours deviated by less than 3 mV from the original value. Even within this small deviation, no trends were discernible.

The presence of this dip in the potential - pH line precludes the measurement of any actual gradient value. However, the overall pH response from pH 8 to 4 is of the order of -40 mV/pH.

Figure 5.2 shows the response of a platinum electrode when transferred between the individual solutions, listed in section 5.2.2, as well as the responses of rhodium and gold electrodes subjected to the same treatment. It is interesting to note that when the electrode is placed in hydrochloric acid (0.1 M), the value

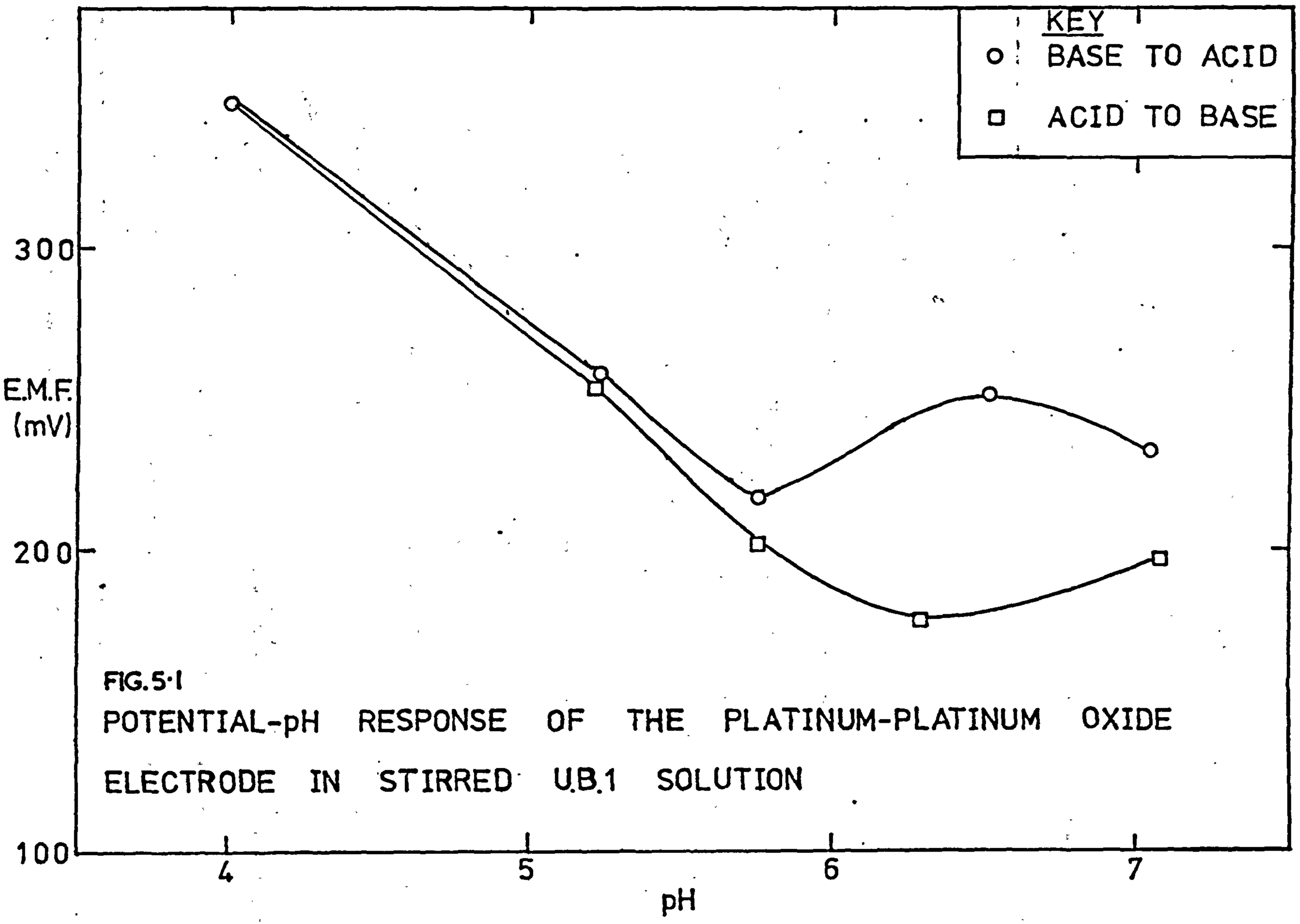


FIG.5·1

POTENTIAL-pH RESPONSE OF THE PLATINUM-PLATINUM OXIDE ELECTRODE IN STIRRED U.B.1 SOLUTION

observed from the unstirred solution is displaced positively by as much as 45 mV over that from the stirred solution. In individual solutions with higher pH values, the discrepancy is far less.

Potential drifts seem to be greatest at low pH values and seem to be far less pronounced for solutions containing Bis-tris than for other solutions.

5.2.4 Rhodium Electrodes

In the course of this investigation, a number of stepwise titrations were carried out using U.B.1 and rhodium electrodes prepared by a variety of methods described in section 5.2.1. The pH responses obtained, even from an individual electrode, varied considerably, e.g. from -44 to -50 mV/pH. The lowest gradients were obtained from the electrode prepared using epoxy resin (-30 mV/pH), while the highest gradients were obtained from the electrode oxidized in fused nitrate for 30 minutes (-57 mV/pH). A decrease in gradient was visible above pH 6 but this was found to be substantially eliminated by permitting the electrode to approach equilibration.

Continuous titration of U.B.1 (from pH 8.9 to 3.3), yielded a straight line with a gradient of -42 mV/pH for an electrode oxidized in nitrate for 1 hour, while the electrode sealed in epoxy resin gave curved plots with lower overall gradients, thus indicating a slower response.

The e.m.f.s obtained from individual solutions are illustrated in figure 5.2. As in the case of the platinum electrode, a

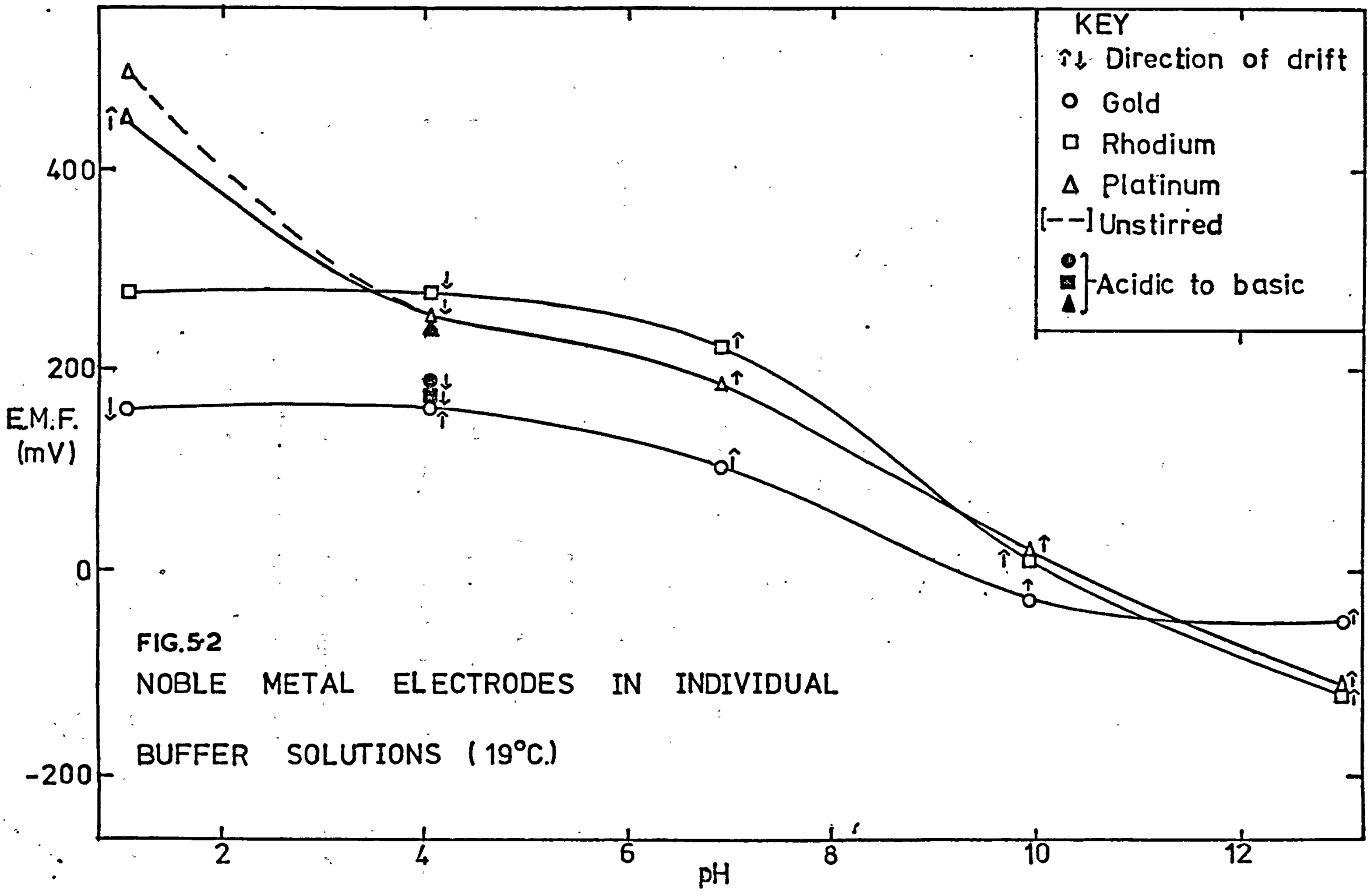


FIG.5-2

NOBLE METAL ELECTRODES IN INDIVIDUAL BUFFER SOLUTIONS (19°C.)

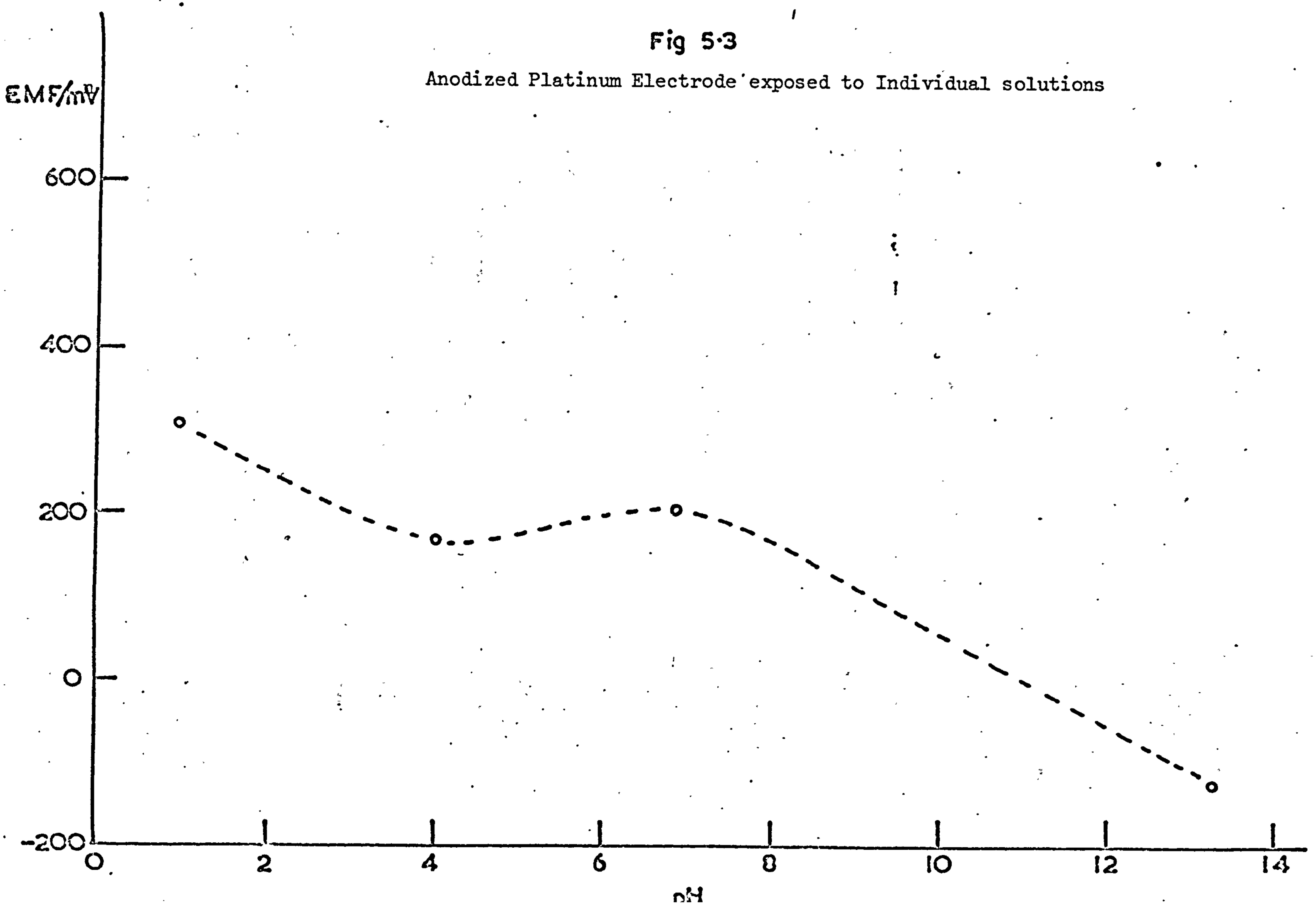
decrease of slope is noticeable between the values obtained from phthalate and phosphate solutions. However, a similar plateau between the values obtained from the phthalate solution and HCl was found to be non-reproducible when the electrode was subjected to these solutions in a different sequence. When an electrode, prepared by anodization was subjected to a similar investigation, a dip like that observed when the platinum electrode was subjected to universal buffer solutions was noticed (fig. 5.3).

The measurement of the e.m.f.s of rhodium-rhodium oxide electrodes was seriously hampered by large, variable drifts. The magnitude and the direction of these drifts appeared to vary with the electrode concerned, with values between 0 and 10 mV/hr. The lowest drifts were observed in the case of the electrode oxidized by anodic polarization, the overall drifts being of the order of 10 mV over the first 2 hours, as opposed to values in excess of 20 mV in other cases. For measurements made using individual solutions, the direction of drifts have been indicated by arrows in the relevant direction. Some of the potential-time plots obtained in this section of this investigation showed the potentials passing through a maximum and then proceeding to drift in the opposite direction. This indicates that more than one electrode process is involved.

Finally, the individual reproducibility of this electrode system is very poor, the potential - pH line passing through pH 7 at various e.m.f. values from -100 to +163mV. This problem is commented on in section 5.3.

Fig 5·3

Anodized Platinum Electrode exposed to Individual solutions



5.2.5 Gold Electrodes

As with the rhodium electrode, this electrode was found to be subject to large, variable potential drifts. The worst example of this effect was electrode A (colloidal gold film), which displayed drifts of the order of -6 to -32 mV over the second hour when subjected to U.B.1 solutions. For this reason, the pH response of this electrode was not examined.

As far as the other electrodes were concerned, there were potential drifts of 0 to 4 mV per hour over the second hour. The magnitude and direction of drift was found to depend on the electrode concerned and even varied from experiment to experiment. It was found that although these drifts are fairly small, taken over a long period of time (e.g. overnight), the electrodes could change by 40 to 50 mV. In general, drifts were greater (3 to 10 mV per hour) at high pH values. Potentials obtained from individual solutions showed larger drifts but the procedure involved the removal of electrodes from solutions which have an effect on the electrode potential.

On account of the suggestion that gold oxide is soluble in acid solution (see section 5.1),[55] in most cases, the investigation has not been extended below pH 4. The potential - pH lines for this electrode system in U.B.1 were, in general, curved and showed poor reproducibility. A lower slope was noticed in the region of pH 6 resulting in a slightly sigmoid curve. Straighter lines were obtained when the electrode was given more time to equilibrate. The gradients obtained varied from +7.5 to -64 mV/pH depending on the electrode and the portion of the pH scale

concerned. Most gradients, however, were above -28 mV/pH.

A continuous titration of U.B.1 applied to electrode D yielded an S shaped curve over the pH range 8.9 to 3.3. The steepest point on the curve was in the region of pH 5 where a 30 mV/pH gradient was observed, while at both extremes, a decrease in gradient from 7 to 9 mV/pH was observed.

Like the platinum and gold electrodes, this electrode (C) was exposed to a series of individual buffer solutions. Figure 5.2 shows the response of the electrode to this treatment. The highest gradient observed was -24.2 mV/pH. At both extremes plateaux were, yet again, evident. Unlike the plateaux observed from the rhodium electrode, this was not affected by rearranging the sequence in which the electrode was exposed to the various buffer solutions.

A brief investigation on electrode D in U.B.1 revealed that the electrode is susceptible to stirring, yielding values from stirred solutions which were measurably more positive than those from unstirred solutions. These differences varied from 4 to 6 mV, above neutrality, to 25 to 30 mV from pH 5 to 4. For individual solutions, however, a variation was only observed when the electrode was subjected to examination in HCl and in this case the difference was insignificant in comparison to those described above.

Finally, the individual reproducibility of these electrodes is once again poor, the potential - pH lines passing through pH 7 at potentials varying from -150 to +237 mV.

5.3 Conclusions

The most striking aspect of the potential - pH response line of the platinum electrode is the pronounced dip. This dip, which is certainly a real effect since it was observed under a variety of conditions, precludes any use of these electrodes for indicator electrode purposes.

It is likely that this effect is due to a redox potential attributable to some couple in the solution. The reduction of oxygen is one likely cause. Since Bis-tris has no apparent effect on the electrode potential, it is difficult to explain why the relative position of the dip on the pH scale was affected by its exclusion and by other changes in procedure. Possibly, changes in solution composition might affect the extent to which oxygen is dissolved in solution, but it is difficult to see why this should cause the above effects. It is, perhaps, significant that changes of slopes in the same pH region are also visible to some extent with the other electrodes investigated in this chapter, particularly with an anodized rhodium electrode.

The response of rhodium electrodes with respect to pH is, in general, fairly close to the theoretical. However, the reproducibility of the gradients obtained is poor. This is undoubtedly associated with the large drifts encountered. The widely differing potentials obtained at pH 7 must again be at least partly due to the drifts observed. It is likely, that a number of problems inherent in the method employed for electrode construction and preparation are mainly responsible.

Firstly, unlike platinum, rhodium metal is quite unsuitable

for sealing into glass. In fact, in the course of this investigation a number of attempts were abandoned because of fracturing of the glass at the glass-metal interface. This effect, which is also referred to in Chapter 7, is mainly due to incompatible coefficients of expansion of the two materials. It is virtually impossible to obtain a seal which is totally impervious to the solution under test. As a result of this, there is a tendency for a stagnant film of liquid to be trapped between glass and metal thus affecting the electrode potential. Also, since rhodium is a very hard metal, the differential expansions will inevitably set up stress effects in the metal, thus impairing the electrode performance.

Secondly, a chemical technique such as that employed in this chapter, will inevitably produce oxide films which vary both in composition and thickness and hence the potentials obtained are more likely to be variable than those obtained from electrodes prepared by electrochemical means.

The changes of gradient and dips observed in some experiments are likely to be of a similar origin to those observed for platinum. Why an anodized electrode should be more prone to this effect is a difficult question to answer. Possibly the thinner oxide films obtained by anodization cause the electrodes to be more susceptible to this effect.

The results obtained from gold electrodes were also of an irreproducible nature and drifting was once again evident. The low slopes obtained from individual solutions, however, cannot be blamed on a slow response since the direction of the drifts observed would tend to enhance and not eliminate this condition.

The apparent change of slope observed at lower pH values in experiments involving individual solutions is likely to be due to Au_2O_3 dissolving in hydrochloric acid (see section 5.1).

In general, it is possible to conclude that none of the electrodes tested merit further study with a view to the production of indicator or pH reference electrodes. However, since continuous titrations using rhodium electrodes yielded straight potential pH lines, a number of further investigations were carried out on electrodes prepared by the deposition of rhodium on platinum blanks. These investigations showed that electrodes prepared in this way have some favourable response and are far more reproducible. The preparation and examination of these electrodes are described in detail in the next chapter.

Chapter 6

DEPOSITED RHODIUM ELECTRODES

It will be recalled that, in the previous chapter, when 'massive' rhodium electrodes constructed from rhodium wire were subjected to comparatively rapid changes of pH, a linear potential change was observed. Apart from defective responses under other conditions, one of the major drawbacks of such a electrode system was an overall lack of reproducibility between individual electrodes. This was presumed to be due, at least in part, to 'stress effects' brought about when this hard metal was exposed to the extremes of temperature involved in sealing the metal into glass, cleaning with hot aqua regia, and oxidation in fused potassium nitrate. Apart from 'stress effects', these extreme pretreatments also tend to result in leakage at the glass-metal interface which also introduces errors. Doubts were expressed as to the feasibility of obtaining films of a consistent composition and thickness by this method.

An attempt has been made to deal with both these problems by electrochemically depositing a mixture of rhodium and rhodium oxide on platinum and rhodium blanks using a special technique described below.

6.1.1 Introduction

Electrodeposits of the platinum group of metals are

characterized by abnormally high hardness and internal stress. Unfortunately, the most striking example of this is rhodium, where the hardness of a deposited sample is in the order of 900 D.P.N. as compared with approximately 120 for the wrought metal.[59] This behaviour is likely to be due to the occlusion in the deposit of basic compounds produced as a result of hydrolysis in the cathode film or in the bulk electrolyte.[59]

In view of the remarks made in the first paragraph of this section, these figures would appear to extinguish all hope of making use of electrodes constructed in this way for pH measurement. However, since the 'active' electrode surface is deposited on 'base' metals already sealed in glass and cleaned with aqua regia, the first two possible sources of stress problems and leakage are eliminated.

Ironically, it is the occlusion of material in the deposited metal which provides a means of eliminating the other two sources of error quoted above. Since the occlusion of oxide in the rhodium metal removes the need for subsequent oxidation, not only is it no longer necessary to heat the electrode assembly to around 400 or 500°C but also a means of obtaining consistent oxide and metal phases is provided.

The presence of oxide in plated rhodium was first reported by McNevin and Tuthill in 1949.[60] These authors attributed this contamination by oxide to the rapid discharge of hydrogen, which increases the pH of the solution in the vicinity of the cathode thus causing hydrolytic precipitation of the rhodium oxide. The precipitation of oxides in this way is quite well known and similar reports of oxide deposits in the case of nickel, chromium and iron

are cited by these authors. If contaminants, such as oxides, are included in the deposit, it will become fine grained and dark in appearance.[61] This is consistent with the observations of these authors.

In 1963, these observations were confirmed by McBryde, Graham and Ott[62] who, like the aforementioned workers, noticed that electroplated deposits of rhodium were considerably heavier than expected and the excess weight was lost if the deposit was reduced by heating in a hydrogen atmosphere. This reduction was found to be accompanied by a change in colour from a dark to light grey. This 'overweight' was found to increase with, but not in direct proportion to, the weight of the deposit.

McBryde et al, however, disagreed with McNevin and Tuthill with regard to the origin of the overweight, questioning the validity of the assumption that the presence of oxide was brought about by the rapid discharge of hydrogen at the cathode. They pointed out that, in experiments carried out under buffered conditions, the proportion of oxide found in the plated rhodium is as high or higher when no hydrogen is evolved as when gassing takes place. Furthermore, it was also pointed out that deposits from buffered solutions show, in nearly every case, a greater "overweight" than those from unbuffered solutions. In view of the greater tendency to hydrogen evolution observed under unbuffered conditions, it is unlikely that the presence of oxides can be attributed to the hydrolytic precipitation resulting from the localized production of alkali.

McBryde et al.[62] suggested that the available evidence supported the hypothesis that oxide contamination is due to the

poor hydrolysis of the complex $RhCl_6^{3-}$ ion to species such as $RhCl_5OH^{3-}$ etc. Increased hydrolysis in buffered solutions would lead to increased oxide production. The suppression of hydrolysis would also explain the observation that the production of oxide is reduced in the presence of concentrated ammonium or sodium chloride. These authors admit, however, that no conclusive proof is available.

It is well known that the current density involved in the deposition of metals is critical to the physical nature of the deposit. At low current densities the discharge of ions occurs slowly, and so the rate of growth of nuclei should exceed the rate at which more are formed. The deposits obtained under these conditions tend to be coarsely crystalline. The rate of formation of nuclei will increase as the current density is raised and the deposit will become more fine grained. At very high current densities, the solution adjacent to the cathode will become depleted of metal ions and consequently, the crystals will tend to grow outwards towards regions of higher concentration to form "trees", nodules or protruding crystals.[61] These phenomena will be discussed with reference to "Stereoscan" photographs in a later section (see section 6.5).

If the current density exceeds a certain limiting value for a particular electrolyte, hydrogen will be evolved at the same time as the metal is deposited. Bubble formation will tend to interfere with crystal growth and hence a porous spongy deposit may be obtained.[62] The limiting value at which hydrogen is produced is known to depend, not only on the electrolyte, but also on the hydrogen overpotential.[62,63] This activation potential, as it

is more correctly called, depends upon the metal concerned and the current density involved.[63] The latter obviously depends on the surface area and McBryde et al.[62] pointed out that surface roughening during electrode cleaning could have an important bearing in this connection. Since the potential at which hydrogen is evolved varies with pH by -59 mV per pH,[63] it is clear that, if desired, hydrogen evolution could be avoided by increasing the alkalinity of the solution.[62] Such changes are apparently associated with an increase in oxide production in this particular case.

A further complication regarding current density has been observed by McBryde[62] who noticed that, when the potential was controlled electronically, the current observed when plating under buffered conditions was prone to adopt a periodic fluctuation, especially after the first 30 minutes. In a typical case, the current would suddenly reach a maximum of 1 A and then gradually fall to zero. This "saw-tooth" current was attributed to the cathode becoming polarized by the deposition of a sparingly conducting layer of oxide. The instrument would then reduce the applied potential until the current fell to zero, when some of the oxide film would slowly dissolve. It must be pointed out that, in this present investigation, at no time was a "saw-tooth" current observed.

As far as the general electroplating of metals is concerned,[61] an increase in temperature has two effects which oppose one another. Firstly, diffusion is favoured, so that the formation of rough or spongy deposits at relatively high current densities is inhibited. Secondly, the rate of crystal growth is increased which favours

a coarse deposit. Increases in temperature also tend to decrease the hydrogen overvoltage, and so favours the evolution of gas as well as the precipitation of hydrous oxides or basic salts. It is, therefore, perhaps significant that McBryde et al.[62] obtained a larger "overweight" from solutions at room temperature than from heated solutions.

The solution recommended by McBryde[62] for the analytical electrodeposition of rhodium consisted of rhodium trichloride dissolved in 100 cm^3 of 3.5 M ammonium chloride to which are added 5 cm^3 of a concentrated buffer solution (3 M acetic acid and 1 M sodium acetate) and 1 g. of ammonium sulphate. It was decided to omit the ammonium chloride since its apparent function is to reduce the quantity of oxide formed. In view of the remarks made at the beginning of this section, this clearly would be undesirable in this particular investigation. The purpose of adding acetic acid and sodium acetate is merely to buffer the solution at pH 4, but the reason for adding ammonium sulphate is less clear. Presumably, it is in some way connected with complex formation.

McBryde et al.[62] suggest the use of a platinum gauze cathode polarized at -400 mV with respect to the saturated calomel electrode (S.C.E.). However, these workers were primarily concerned with the separation of rhodium and iridium and achieving complete deposition. In the present work, a platinum wire sealed in glass was substituted. This metal was used since platinum permits good glass-metal seals to be obtained. At a later stage, rhodium wire electrode bases were again employed, since the use of a lead glass interface between the rhodium metal and soda glass enabled satisfactory seals to be obtained. The reasons for

reverting to rhodium blanks will be discussed in a later section.

The same authors suggested that spectrographic carbon should be employed as an anode, since platinum showed a tendency to dissolve in the presence of 3 M ammonium chloride. It was decided to use a platinum counter electrode in this investigation on the grounds that this constituent would be omitted from the plating solution. However, as a result of X.P.S. measurements (discussed later), a carbon secondary electrode was used to prepare electrodes for some of the final experiments (see Table 6.1).

In this section, the overweight observed during the deposition of rhodium has been explained by the contamination of the rhodium deposit with oxide. This assumption has been made solely on the basis of conclusions made in the two papers concerned. Although both groups of workers have succeeded in reducing this overweight, no conclusive evidence is presented to show that the deposit is indeed a mixture of rhodium and an oxide. It seems likely that, at the potentials employed, any oxide formed would be electrochemically reduced.[64] It is feasible that some chlorinated species may be incorporated with the rhodium and it is this, rather than the oxide which accounts for the overweight.[64]

Another unknown which would interfere with the use of electrodes constructed in this way would be the identity of the oxide concerned, assuming that an oxide is in fact present. As stated in Chapter 5, the only stable oxide of rhodium is Rh_2O_3, although dermisorbed oxides ($Rh(O)_x$) have been reported. It is possible that the mechanism by which the oxide is produced could offer some possibilities as to the chemical nature of the

oxide. It was suggested, at first, that the oxide was due to a hydrolytic reaction caused by the evolution of hydrogen, but McBryde has put forward reasons why this should not be so and has advanced an alternative hypothesis (previously mentioned). If either scheme were true, it is likely that a chemically formed oxide would result (Rh_2O_3).

Another possibility, that oxygen present in solution could be occluded in the metal deposit would result in the formation of a non-stoichiometric oxide (mentioned above). Possible electrode reactions for both oxides are given in Chapter 5.

Clearly, it is desirable that the chemical nature of various electrode phases, as well as any contaminants, should be known. To this end, a number of experiments were carried out making use of a technique known as X.P.S. or E.S.C.A. This technique will be dealt with later in this chapter.

The optimum plating potential was given by McBryde[62] as -400 mV with respect to the S.C.E. In view of the less than ideal cell chosen for deposition in this investigation, it was decided that it would be prudent to examine polarograms, obtained using this cell, in order to verify this observation.

The next section of this chapter refers to work originally carried out for this purpose alone; however, some other interesting points came to light during its compilation and these are also mentioned.

6.1.2 Determination of Optimum Plating Conditions

Theory

In the original paper by McBryde et al.[62] the optimum plating conditions were stated. As was stressed in section 6.1.1, these were selected in order to enable pure, oxide-free rhodium to be obtained. Clearly, in this work, it is desirable that a substantial quantity of oxide should be deposited along with the rhodium metal.

In the aforementioned paper, it was suggested that ammonium chloride should be added, in order to restrict the quantity of oxide produced. As was indicated in the previous section, it was decided to eliminate this component from the solution employed in this investigation. Therefore, the modified plating solution used was composed as follows:

5 cm^3 of a concentrated buffer containing (3 M acetic and 1 M sodium acetate)

1 g Ammonium sulphate

0.25 g Rhodium trichloride

These materials were diluted to 100 cm^3 with distilled water. The sample of rhodium trichloride was described by the suppliers (B.D.H.), as $Rh_2Cl_3.xH_2O$, therefore, it must be pointed out that the quantity 0.25 g, quoted above, relates only to this particular consignment.

The plating potential of -400 mV, with respect to the S.C.E., quoted in the previous section, was considered to be adequate as far as the initial assessment of this system as a pH electrode was concerned. However, before attempting a more detailed

investigation of the electrode system, it was considered essential that some first-hand knowledge of the current-potential relationships involved during the electrolysis of this solution, should be gained.

It is customary for polarographic measurements to be made using rotating disc electrodes and to a lesser extent rotating wire and vibrating wire electrodes. These devices are adopted in order to overcome mass transfer effects. To understand these effects, it is first necessary to consider the processes involved at an electrode.[65]

The general reaction:

$$Ox + ne \rightarrow Red \qquad 6.1$$

involves the individual processes:

$$(Ox)_{Bulk} \rightarrow (Ox)_{Electrode} \qquad 6.2$$

$$(Ox)_{Electrode} + ne \rightarrow (Red)_{Electrode} \qquad 6.3$$

$$(Red)_{Electrode} \rightarrow (Red)_{Bulk} \qquad 6.4$$

The first two equations are processes with finite rates and, in an electrical sense, reactions in series.[65] Voltametric current, i.e. the overall flow of electrons, can be limited by either reaction. The rate of the electron transfer reaction 6.3 is an exponential function of the applied potential, therefore, in most cases, the rate of this process is very rapid in comparison to that of process 6.2. Therefore, the overall current is limited by the slower of the two processes i.e. the mass transfer of the

oxidized species from the bulk solution to the proximity of the electrode concerned. Under normal circumstances such a reaction is diffusion controlled (see later). Reactions such as these are said to be mass transfer controlled.

If the rate of mass transfer is increased to a very high value, so that it exceeds that of electron transfer, the reaction will become charge transfer controlled. Under these conditions, the kinetics of electron transfer can be studied if desired. Charge transfer controlled conditions can be achieved merely by stirring the solution, however, in most cases, the techniques mentioned above are adopted as they enable mathematical models to be derived. Simple stirring techniques, on the other hand, tend to cause turbulence and so are normally avoided.

Since the main object of carrying out a simple polarographic investigation was to determine the optimum plating potential to be employed in the production of electrodes intended for subsequent pH measurement, it was decided to duplicate the actual plating conditions exactly. For this reason, identical cells were used for both stages of the work. This decision meant that the polarized electrode had to be a stationary wire electrode suspended in an unstirred solution. Furthermore, any advantages derived from employing specialized electrode systems would hardly justify the expense and time consumed in the construction of rotating disc electrodes. It was realized, of course, that the results obtained from these experiments would only be of use in this particular investigation and would have no general significance.

Three mass transfer processes are normally encountered in

polarography namely: migration, convection and diffusion.[65]

Migration is a result of the force on charged particles exerted by an electric field. In the presence of a large excess of supporting electrolyte migration is minimized sufficiently to be neglected.

The term convection implies mass transport induced by stirring. It can be caused by thermal, mechanical or other disturbances within the solution. Natural convection develops spontaneously in any solution undergoing electrolysis since density differences occur near the electrode. This form of mass transfer is particularly important at vertical electrodes such as those used in this work.[66] Forced convection is the term applied in the case of externally agitated solutions.

Lastly, diffusion takes place whenever concentration differences are established. Since a concentration gradient develops as soon as electrolysis is commenced, this mode of mass transport plays a part in every electrode reaction.

In this investigation, it is not of prime importance which mass transfer mode predominates. It is more important to realize that these effects are present, as this will facilitate the interpretation of the results, obtained both in this and a later section. In actual fact, it is likely that both convection and diffusion take place.

Apparatus

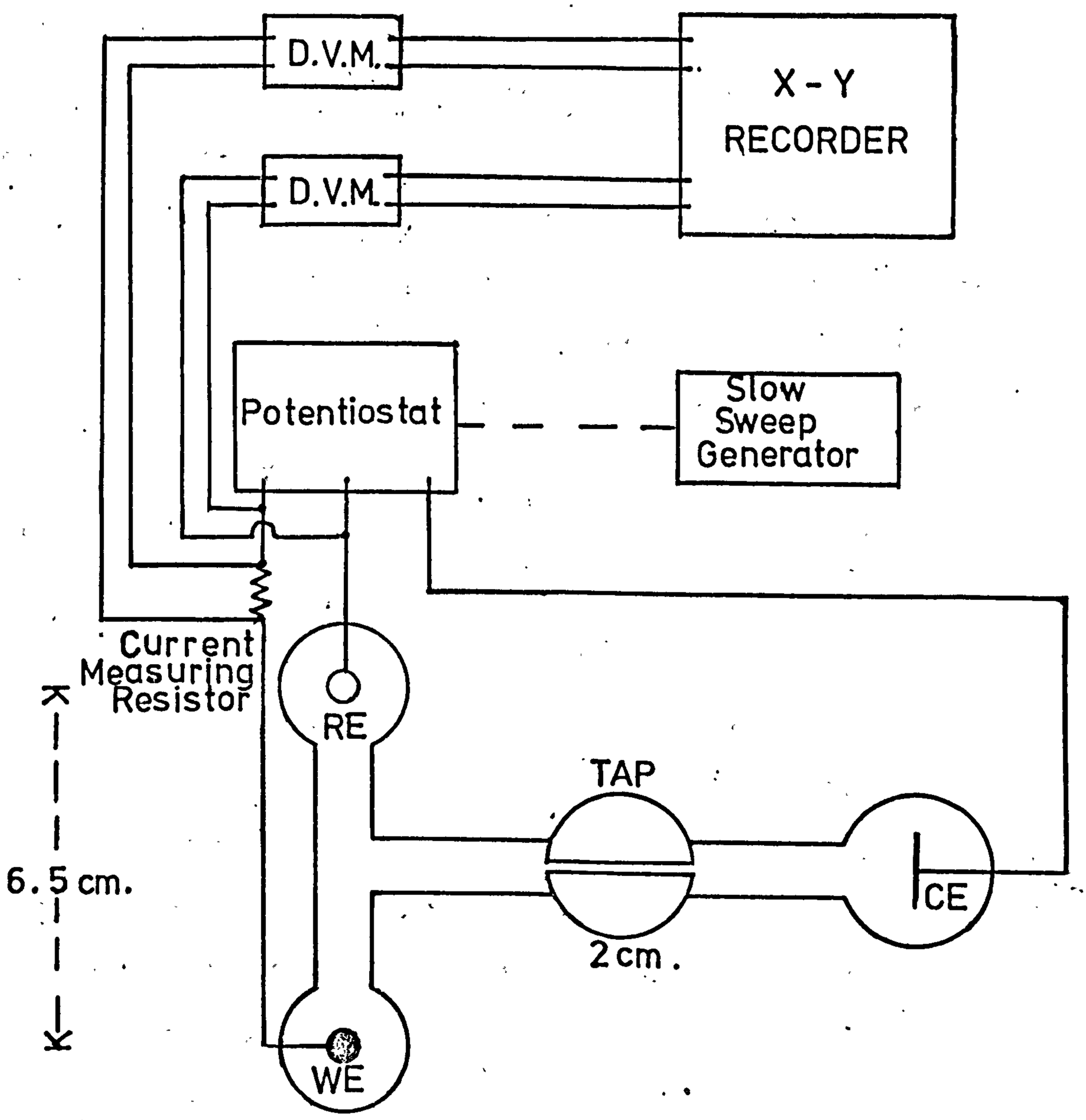
The experimental work reported in this section was carried out using a potentiostat and slow sweep generator, both constructed

by the School of Chemistry Electronic Workshop. The arrangement of apparatus (fig. 6.1), apart from the inclusion of the sweep generator, corresponds exactly to that employed for electrode deposition. It was, of course, realized that a substantial ohmic drop (IR drop) would result from this arrangement but this is insignificant since the prime object of carrying out potential sweeps was to discover the 'ideal' plating potential for this cell. A conventional three electrode cell constructed in pyrex glass was employed for these measurements as shown in the diagram.

The reference electrode was a Radiometer S.C.E., Type 401, as described for pH measurements in Chapter 2. The working electrodes were platinum and rhodium wires 1.5 cm. in length, sealed into glass. In the former case, wires with a diameter of 0.72 cm. were used while in the latter case, wires 0.52 cm. in diameter were used. The secondary (or counter) electrode took the form of a platinum spade, 1.0 cm. by 1.0 cm., spot welded on to a platinum wire, which was,in turn, sealed into soda glass. In accordance with general practice, a secondary electrode with a much larger area than the working electrode was chosen. This was to ensure that any polarization effects observed were taking place at the working electrode and not the secondary. As can be seen from the diagram, the secondary electrode was housed in a separate cell chamber in order to prevent the products of reactions at this electrode interfering with the working electrode. Connections to both secondary and working electrodes were made by means of mercury contacts.

FIG.6·1

SCHEMATIC DIAGRAM OF APPARATUS FOR SIMPLE POLAROGRAPHIC EXPERIMENTS



Procedure

Both the secondary and working electrodes were cleaned by immersion in hot aqua regia before each experiment. Prior to this, any excess surface deposits were removed by abrasion with very fine grade emery paper (Grade 2/0). After cleaning, each electrode was washed with distilled water and then stored temporarily in distilled water. The purpose of applying cleaning procedures is to destroy by oxidation any organic materials on the surface (including grease, dust etc.).[67] The use of aqua regia for this purpose offers the added advantage of removing any finely divided platinum present. Unfortunately, these cleaning procedures involve the use of powerful oxidizing agents, and consequently there is a tendency for electrode surfaces to become oxidized. In this case, however, this is not of great importance since the cleaning time was restricted to around 10 to 20 seconds, and as cathodic polarization is involved any deposit is likely to be reduced, although such reduction can take a very long time.

The apparatus was set up as shown in figure 6.1. No special precautions were taken regarding solution temperature, the experiments being carried out at ambient temperature ($20^{o}C \pm 3^{o}C$). Similarly, atmospheric oxygen was not excluded since it was not excluded during the preparation of electrodes for pH measurements, and in fact, dissolved oxygen could play an important part in the production of the oxide phase, since oxygen can be electrochemically active.

In the first instance, linear potentiostatic cathodic potential

sweeps from the rest potential were undertaken with the relatively slow sweep rate of 3 mVs^{-1}. It was found, however, that this resulted in polarograms with all the information restricted to the extreme right hand side. Consequently, the polarograms displayed in figures 6.2 and 6.3 refer to cathodic sweeps from 0 mV with respect to the S.C.E.

The current-potential curves shown in these figures were plotted by means of a Bryans X-Y recorder (21000). The procedure was repeated for platinum and rhodium electrode blanks. A number of anodic sweeps at the same rates were also attempted in the case of the rhodium electrode blank. In this case the solution employed was aqueous sulphuric acid (0.1 M).

Results and Inferences

The polarograms illustrated in figures 6.2 and 6.3 relate to the 2nd and 11th cathodic sweeps respectively on platinum and rhodium wire electrodes. On figure 6.3, plateaux corresponding to the limiting current associated with the deposition of rhodium can be clearly discerned from approximately -375 mV w.r.t. the S.C.E. Limiting currents of about -104 μA and -72 μA and residual currents of -52 μA and -24 μA (at -200 mV) can be measured for the platinum and rhodium 'bases' respectively. However, these have no bearing in reality since the measured currents refer to electrodes of unknown area and, since the surface areas are likely to increase as more material is deposited, it would be futile to attempt a measurement.

It can be seen from the figures illustrated that a greater

FIG.6·2

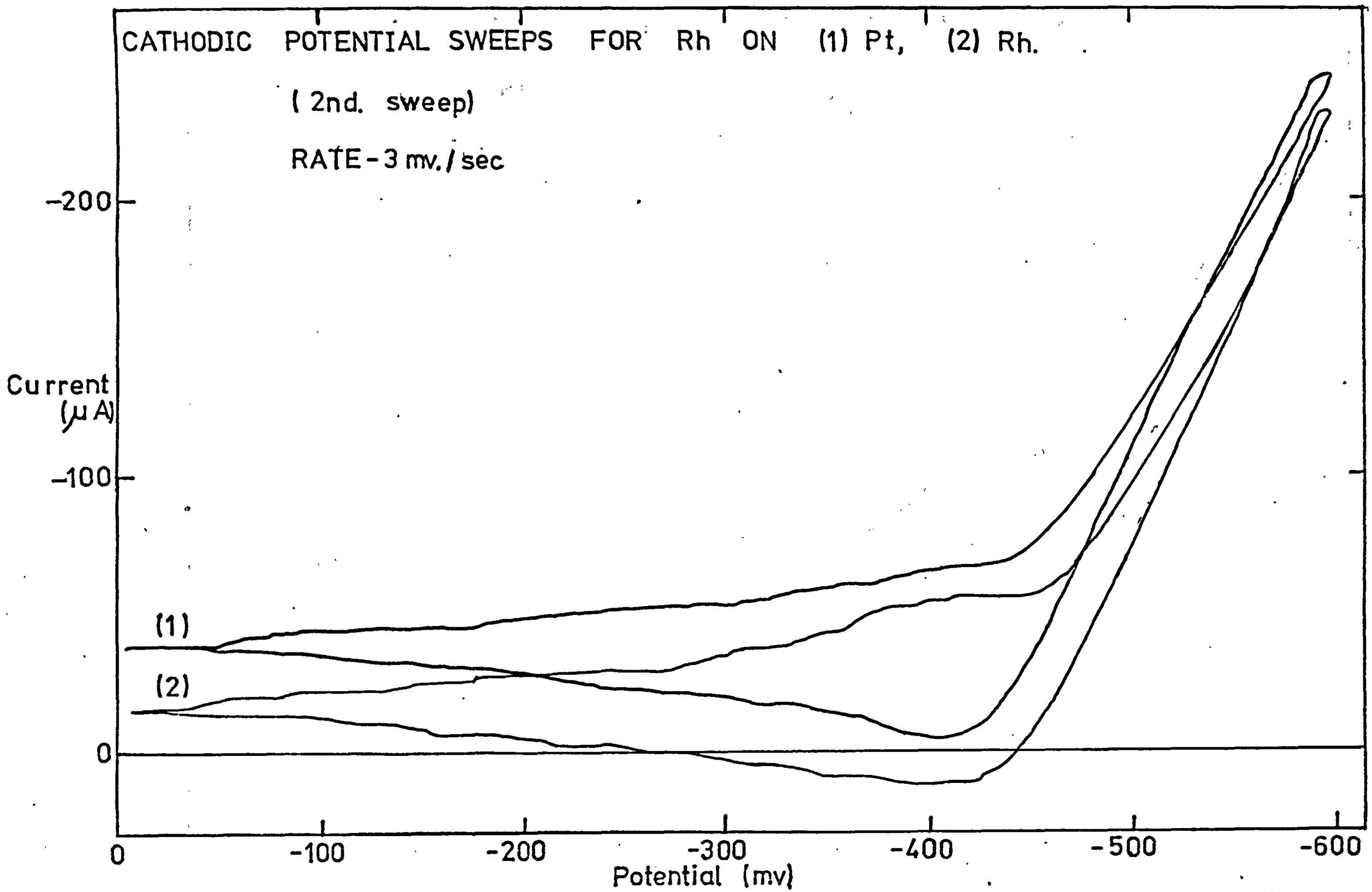
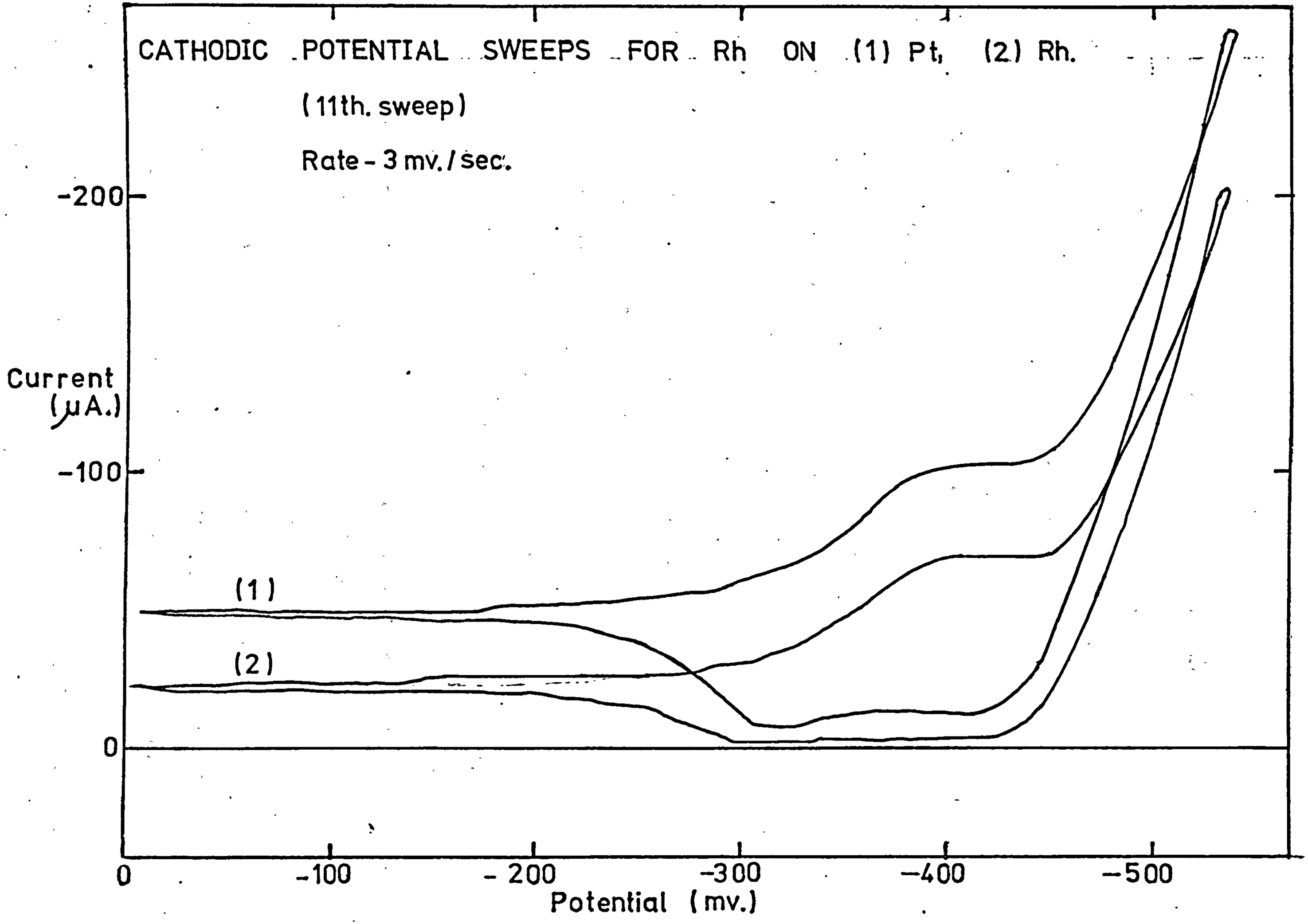

CATHODIC POTENTIAL SWEEPS FOR Rh ON (1) Pt, (2) Rh.
(2nd. sweep)
RATE - 3 mv./sec
-200
Current (μA)
-100
(1)
(2)
0
0
-100
-200
-300
-400
-500
-600
Potential (mv)

FIG.6·3


CATHODIC POTENTIAL SWEEPS FOR Rh ON (1) Pt, (2) Rh.
(11th. sweep)
Rate - 3 mv./sec.
-200
Current (μA.)
-100
(1)
(2)
0
0
-100
-200
-300
-400
-500
Potential (mv.)

current passes in the case of the platinum blank than in the case of the rhodium blank. This is due to a greater surface area in the former case. It can also be seen that at the upper potential limit forward and reverse sweeps overlap. This is indicative of a changing surface area, as suggested above.

The most useful aspect of these results lies in the fact that a clear indication is given of the potential range over which rhodium is deposited. It is clear from the illustrated polarograms that deposition commences around -300 mV w.r.t. the S.C.E. and it can be deposited over potentials up to a value between -420 and -440 mV where hydrogen evolution commences, (deposition does not stop at this value of course). This compares with a literature value of -500 mV for acetate buffer solutions at pH 4[63]. Clearly, the close proximity of the potentials at which rhodium is deposited and hydrogen is liberated could present problems which will be discussed in a later section of this chapter.

Fig. 6.2, which illustrates a 'second sweep' polarogram, taken over a slightly wider potential range, shows that, although the polarograms obtained using both metal 'bases' are virtually identical, a vestigial plateau is apparently visible in the case of rhodium. Possibly, this may be due to easier crystal nucleation in the case of rhodium. In addition, when a platinum base was used, six consecutive sweeps were necessary before the lines of the polarogram became closely grouped in the 'plateau' region. When a rhodium 'base' was substituted, however, this effect was much less pronounced although the lines did move closer together with each successive sweep.

Earlier in this section, the significance of the terms

'mass transfer controlled' and 'charge transfer controlled' were discussed within a polarographic context, along with various modes of mass transport. It is likely that, under unstirred conditions, the reaction will be mass transfer controlled, in particular by the processes of convection and diffusion. However, a superficial examination of the polarographic wave seems to suggest that this is, in fact, not the case as the curve bears a greater resemblance to that expected from a charge transfer controlled reaction.[68] The polarograms show, in both cases, a slow increase in current as the potential becomes more cathodic. At higher potentials, the chemical reaction increases and a greater current is observed. The flow of current eventually causes concentration polarization and in the 'plateau' region the current is virtually diffusion controlled. This plateau apparently becomes more pronounced with each successive sweep.

The inference that the process is charge transfer controlled is reinforced by the observation that, when the log of the difference between residual and current was plotted against potential, Tafel slopes of 110.5 and 112.5 mV/decade were obtained for the platinum and rhodium bases. These values are far in excess of those expected for 1 electron mass transfer controlled processes (see section 6.1.5). It must be pointed out, however, that the cell used for these measurements has a large unknown resistance. It is, therefore, quite conceivable that the ohmic connection might be sufficiently large to conceal Tafel slopes characteristic of mass transfer controlled processes.

Other authors[69] have stated that, for the overall three electron reduction Rh (III) to the metal, 60 mV per decade were

observed and these were interpreted by a 1 electron mechanism involving an unstable Rh (II) intermediate.

Finally when a rhodium blank was polarized anodically a different collection of peaks was obtained with each sweep. For this reason, all such attempts were quickly abandoned.

6.1.3 Preparation of Electrodes

In the last section, it was suggested that the plating potential of -400 mV, with respect to the Saturated Calomel Electrode mentioned by McBryde et al.,[62] would be appropriate for the initial assessment of such electrodes for pH measurements. Most electrodes referred to in this chapter were prepared at this potential, although in some cases other plating potentials were employed in order to discover whether or not the potential-pH behaviour could be altered by this means.

Electrode 'blanks' were prepared from a) platinum wire sealed into soda glass tubing, and b) rhodium wire sealed into soda glass tubing by means of an interface of lead glass. The latter permitted the expansion of the metal within the glass seal since the roughly comparable coefficients of comparison of rhodium and lead glass were more compatible than those of rhodium and soda glass. The other electrodes employed as well as the glass cell were identical to those described in section 6.1.2.

At first, electrical connection to the test electrodes, both at this and subsequent stages, were made using shielded copper wires dipping into pools of mercury inside the glass tubing. It was found, however, that the well known solubility of copper

in mercury was sufficient to cause the copper wire to become saturated with mercury. After a period of time, the wire became permeated over its entire length, and eventually drops of the liquid metal were seen emerging from the coaxial connections at the junction box.

As a result of this observation a number of alternatives were tried. Conducting epoxy resin (Hysol K20) was found to be suitable for temporary repairs but was too difficult to manipulate for general use and connections made in this way tended to disintegrate if subjected to too much flexing. Wood's metal ($70^{o}C$), dropped inside the tube, and then warmed until molten using a hairdryer, was found to be acceptable for platinum blanks. In the case of rhodium blanks, however, this was not so, since it was found that most attempts resulted in cracking at the lead glass-soda glass interface. The answer to this problem was eventually found to lie in spot welding a length of copper wire to the rhodium prior to sealing in glass. Shielded copper wire could then be soldered into place at the open end of the glass tube. A piece of flexible plastic tubing pushed over the top of the glass tube gave the arrangement a certain degree of rigidity, thus preventing flexing at the solder joint and subsequent breakages. Prior to depositing the metal each electrode blank was subjected to the cleaning procedure described in the previous section and stored briefly in distilled water.

The plating apparatus was set up as shown in figure 6.1 with the exception of the Slow Sweep Generator which was omitted. The plating solution was made up as specified in section 6.1.2, that is, rhodium trichloride was dissolved in 100 cm^3 of distilled water

to which were added 5 cm^3 of a concentrated buffer solution (3 M acetic acid, 1 M sodium acetate) and 1 g. of ammonium sulphate.

Plating was carried out at ambient temperature in all cases and no attempt was made to exclude atmospheric oxygen as this could be involved in the process of oxide 'contamination'. In most cases, plating was continued for 1½ hours, however, the duration was varied on some occasions. These are listed for each electrode prepared, along with the plating potential, in Table 6.1. After the required time had elapsed, the electrode was removed without interrupting the current and then washed and stored under distilled water.

As reported in section 6.1.1, the results of work carried out using the X.P.S. technique (section 6.5) showed some indication of contamination with platinum on some of the samples. For this reason a carbon anode was substituted in later experiments. These are indicated by the letter (C) in the relevant column of Table 6.1.

It was also observed that a gradual change in colour of the plating solution from a dark red-brown to yellow took place over extended periods of time. It was first thought that this colour change was, in some way, related to the presence of ions containing platinum. It proved impossible to detect the presence of this metal by the chemical methods suggested by Mellor[70] owing to the overwhelming excess of rhodium in solution. It was later discovered, however, that this colour change was observable even in solutions which had not been exposed to platinum anodes.

Other explanations for this change of colour include the

Table 6.1

Notation	Plating time (mins.)	Type of electrode blank	Anode	Potential (w.r.t. SCE) (mV)	Length x diameter (wire) (cms.)	Dimensions ('spade') (cms.)
A1	90	Pt wire	Pt	-400	1.5x0.040	
A2	90	Pt wire	Pt	-400	1.5x0.040	
A3	150	Pt wire	Pt	-400	1.5x0.040	
B1	150	Pt wire	Pt	-400	1.5x0.040	
B2	150	Pt spade	Pt	-400		0.5x1.5
C1	90	Pt wire	Pt	-358.9	1.5x0.072	
C2	88	Pt wire	Pt	-382.7	1.5x0.072	
C2[1]	90	Pt wire	Pt	-382.7	1.5x0.072	
C3	90	Pt wire	Pt	-400.0	1.5x0.072	
C4	90	Pt wire	Pt	-430.7	1.5x0.072	
C5	90	Pt wire	Pt	-454.4	1.5x0.072	
C6	90	Pt wire	Pt	-478.4	1.5x0.072	
D1	90	Pt wire	Pt	-400	1.5x0.072	
E1	90	Pt wire	Pt	-400	1.5x0.072	
E2	90	Pt wire	Pt	-400	1.5x0.072	
E3	90	Rh wire	Pt	-400	1.5x0.052	
E4	90	Rh wire	Pt	-400	1.5x0.052	
F1	90	Pt spade	Pt	-400		0.5x1.5
F2	90	Pt spade	Pt	-400		0.5x1.5
F3	90	Pt spade	Pt	-400		0.5x1.5
F4	90	Pt spade	Pt	-400		0.5x1.5
G1	30	Rh wire	C	-400	0.95x0.0515	
G2	90	Rh wire	C	-400	0.9x0.0512	
G3	155	Rh wire	C	-400	0.8x0.051	
G4	98	Pt wire	C	-400	1.0x0.0733	

effects of pH and light. Experiments involving the addition of acidic and alkaline solutions indicate that variations of pH are not the cause and the effect of light seems a more likely alternative.

Alternative explanations for the detection of platinum will be given in section 6.5.

6.1.4 Potential - pH Measurements

As with the other electrodes investigated, most potential - pH measurements undertaken on this system made use of a universal buffer solution (U.B.4).

When electrodes of this description were subjected to a 'stepwise'-pH examination, pronounced drifting of potential was noticed at all pH values. The net result of this effect was a steep potential - pH slope above pH 5 to 6 and a smaller gradient at lower pH values. The values of these gradients and the general shape of the response line obviously vary with the time allowed for equilibration. This is illustrated by the observation that, although the slope observed above pH 6 seems to be consistent at -78 to 79 mV/pH, the gradient below pH 5 varies from -48 to -66 mV/pH (Figure 6.4). However, values taken under controlled temperature after a standardized period of 20 hours, show a pH response line which has three distinct segments (see figure 6.5). The direction of potential drift is indicated by arrows on both figures.

Figure 6.5 also illustrates the effect of varying the potential at which the rhodium deposit was electroplated. The

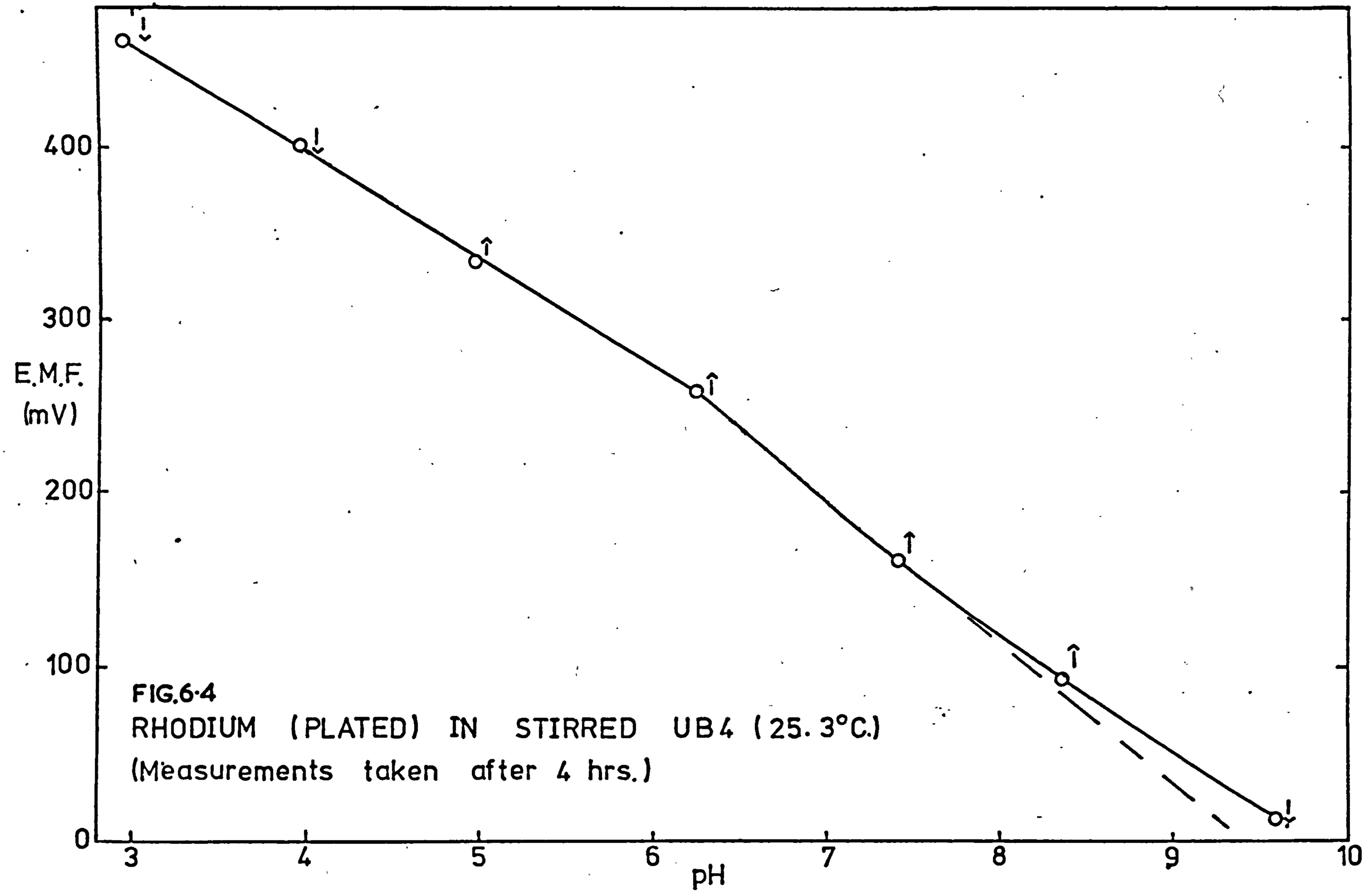


FIG.6-4
RHODIUM (PLATED) IN STIRRED UB4 (25.3°C.)
(Measurements taken after 4 hrs.)

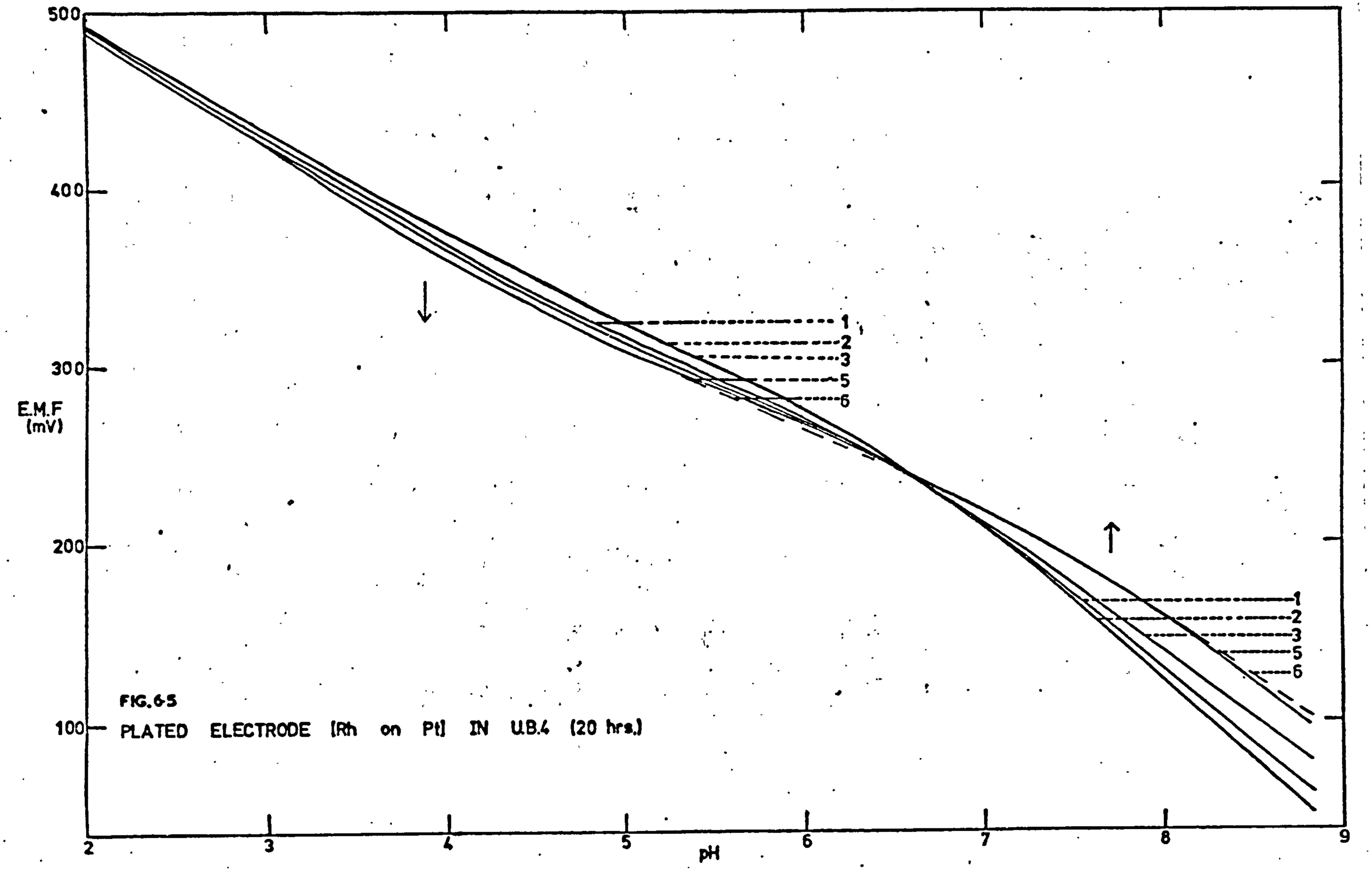


FIG. 6-5
PLATED ELECTRODE [Rh on Pt] IN U.B.4 (20 hrs.)

numbers shown on the diagram correspond to those referred to as C1, C2, and so on, in Table 6.1.

The gradients observed on the figure vary according to the electrode in question. At very low pH values, the observed gradient varies from -61 mV/pH for electrode C2 to -66 mV/pH for electrode C5. It is impossible to quote gradients for the other regions of the pH scale since the pH response lines are curved. Instead, the figures quoted below relate to the apparent minimum potential change over one pH unit. For the pH range 5 to 6, electrode C5 displays a minimum gradient of about -45 mV/pH, while at the other extreme, for electrode C2 a minimum of approximately -50 mV/pH can be measured in the same pH region. The same difficulties in slope measurement are also encountered at higher pH values. These gradients vary from a value in excess of -66 mV/pH, in the case of electrode C6 to a value in excess of -90 mV/pH, in the case of electrode C2.

Since the members of the 'C' series of electrodes differ only in terms of the plating potential used in their preparation, it would be reasonable to expect any observed difference in pH response to bear some form of correlation with plating potential. However, on examination no such relationship can be found. Instead of this, at pH 9, widely separated potentials, arranged in no apparent order, are obtained. It is found that the separation between these potentials is reduced as the pH decreases until the potential - pH lines cross around pH 6-5. The 'crossover point' in figure 6.5 was determined by means of the points. It is easy to see that this point could, in fact,

coincide with neutrality. On the acid side of neutrality, it is found that the separation increases once more, but to a lesser extent, with the potentials arranged in the reverse order to that observed under alkaline conditions.

If, however, the potentials observed at each pH value are plotted against deposition potential (fig. 6.6), one possible reason for the unexpected order in which the potentials from the various electrodes are arranged, comes to light. From Faraday's laws the mass of metal deposited, and consequently its thickness, will increase as the quantity of electricity passed is raised. Therefore, any increase in potentials, below that at which the limiting current operates (see figure 6.3), will result in a corresponding increase in current and hence an increase in the thickness of the deposit. At potentials where the limiting current operates, the thickness of the film obviously cannot grow with increasing potential, but any increase of potential will cause the deposit to become increasingly flaky as the amount of hydrogen produced at the electrode increases (see section 6.1.1). This observation was verified visually, the deposits prepared at higher potentials having a black 'loose' appearance rather than the dark grey of those prepared at lower potentials.

Since platinum is a well known catalytically active metal, it would seem likely that any exposed platinum might affect the potentials recorded from a particular electrode. The electrodes with the flaky, porous surfaces would obviously be particularly prone to any effect of this sort. (Evidence of porosity, in general, is given in sections 1.5 and 5 of this chapter). Electrodes with thinner deposits would be similarly affected,

but to a lesser extent. The fact that performance is drastically affected by exposure of the platinum surface is demonstrated by the behaviour of C4, an electrode with a rhodium film which had been previously mechanically damaged exposing a substantial area of platinum (see figure 6.6, not shown on figure 6.5).

If this hypothesis is correct, then the platinum should have least effect on the electrode prepared by plating at a potential on the linear portion of the polarographic wave (illustrated on figure 6.3), close to the potential at which the limiting current begins to operate. This is, in fact, found to be so (see figure 6.6). This explanation accounts for the order in which the potentials of the electrodes appear, but does not explain the reversing of this order around neutrality. Furthermore, this explanation does not satisfactorily explain the general sigmoid shape of the potential - pH line, neither does it account for the large drifts encountered at certain pH values. It is, therefore, not proven conclusively but merely put forward as one of a number of possible inferences.

In view of the complex nature of the potential - pH behaviour of this electrode system, under normal circumstances, this electrode would have been discarded. However, it was found that, when the technique of continuous titration (described in Chapter 3), was applied, much more promising results were obtained. Figure 6.7 shows the behaviour of the 'C' series of electrodes when subjected to U.B.4 solution (30 cm^3), titrated with hydrochloric acid (0.1 M). Each electrode was allowed to stand for 3 hours prior to titration, in order to eliminate complications due to the initial transient observed on introducing electrodes to the solutions. The

FIG.6·6

E.M.F. IN U.B.4 vs DEPOSITION POTENTIAL

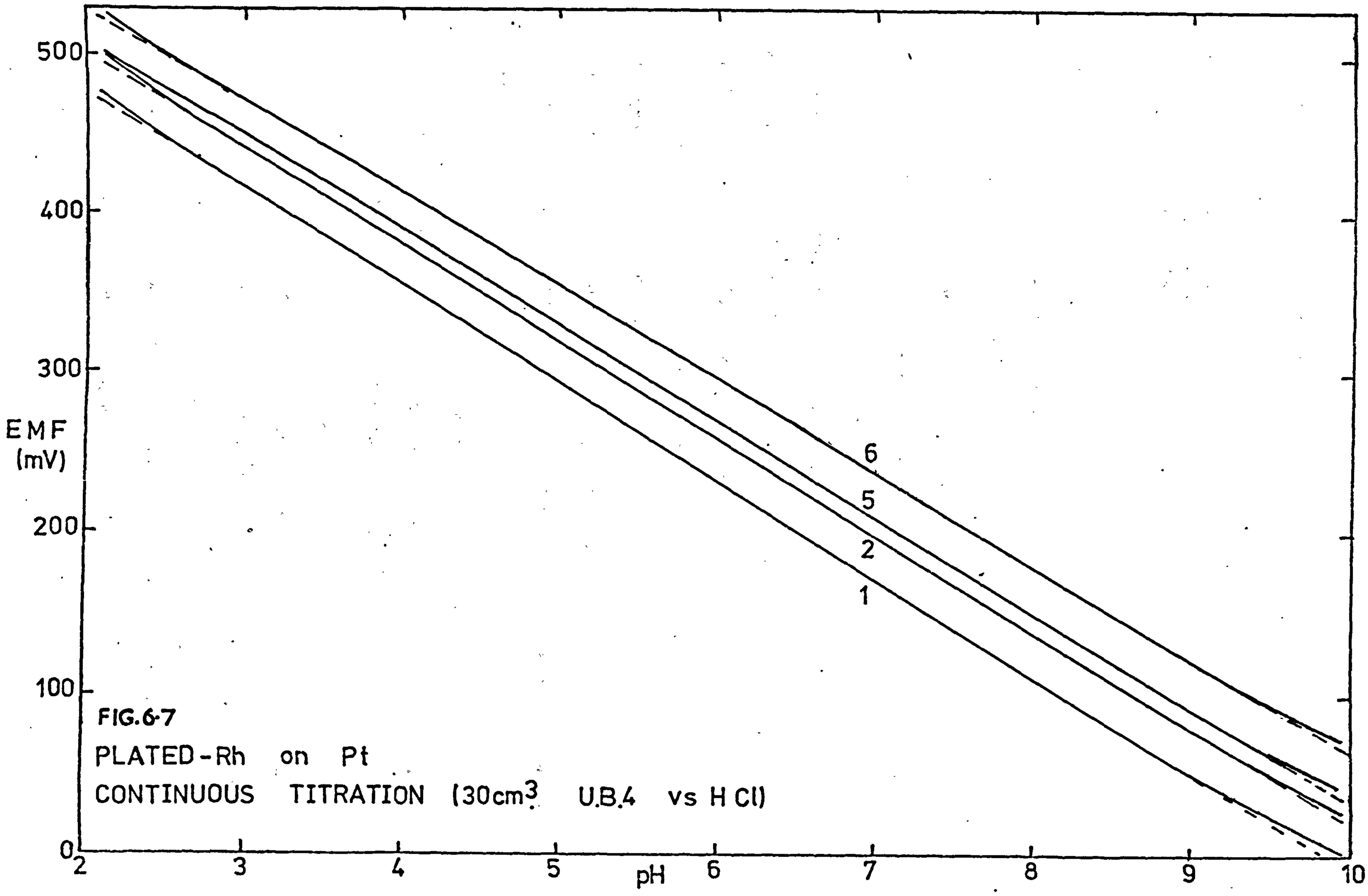


FIG.6-7

PLATED-Rh on Pt

CONTINUOUS TITRATION (30cm^3 U.B.4 vs H Cl)

potential - pH lines obtained in this way have gradients from -59 to -60 mV/pH. These slopes are close to the values expected for a 1 electron reaction at 25°C. Because of this apparently theoretical 'immediate' response, the investigation of this system has been expanded in order to determine the nature of the interferences, and thereby investigate the possibility of their elimination.

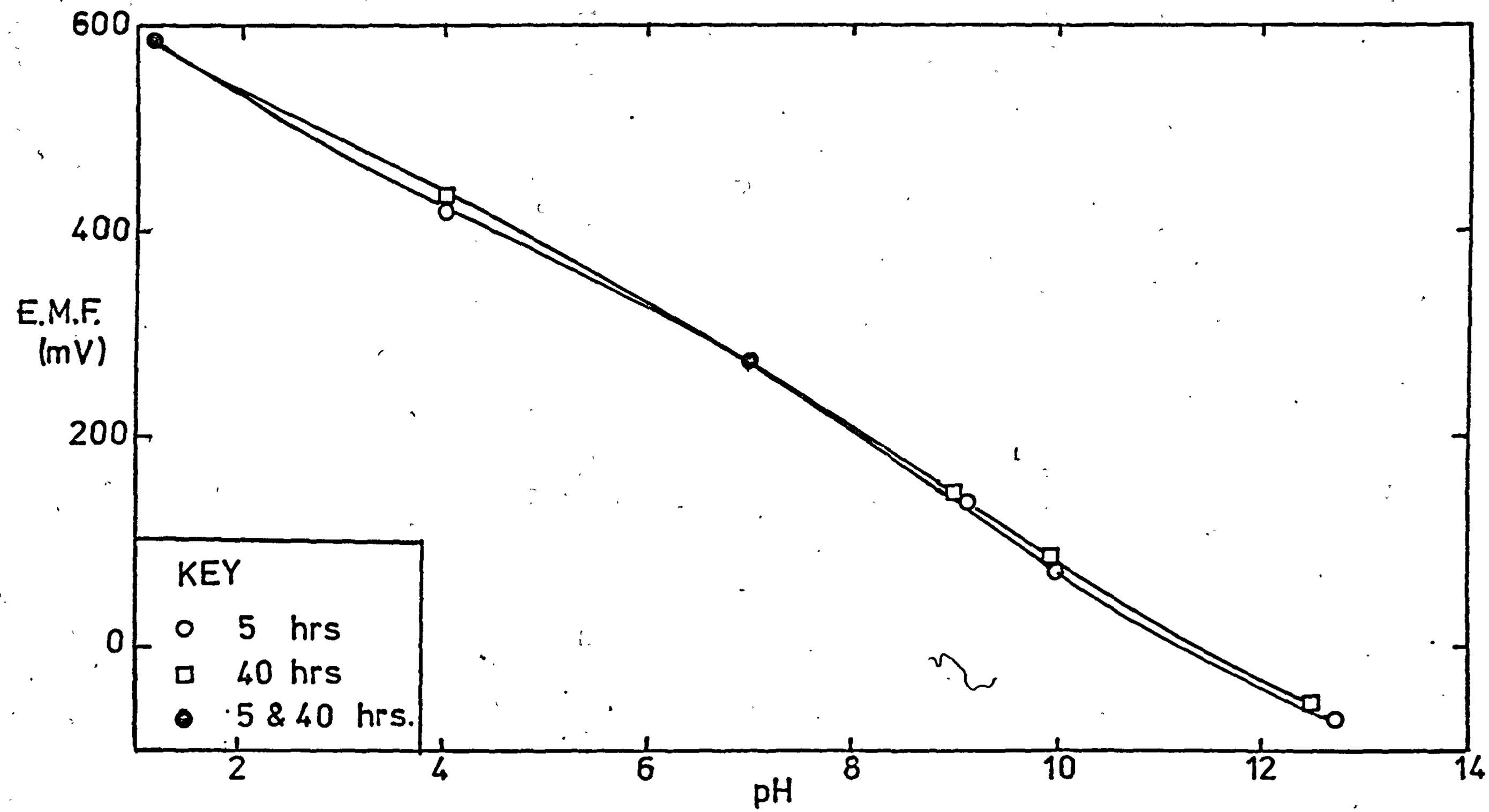
The attractiveness of this system as a pH electrode is enhanced by its behaviour when subjected to a number of individual 'non-amine' solutions over the pH range 1 to 12. These solutions were as follows: potassium hydrogen phthalate (0.05 m), a mixture of disodium hydrogen phosphate (0.025 m) and potassium dihydrogen phosphate (0.025 m), sodium carbonate (0.025 m) and sodium bicarbonate (0.025 m), sodium tetraborate (0.01 m), hydrochloric (0.1 M), sodium hydroxide (0.1 M). Not only does the graph obtained for electrode C3 using these solutions show a less pronounced sigmoid character, but also, the points obtained apparently move closer to the linear conditions as time progresses (see figure 6.8).

The latter observation is completely at variance with that made using U.B.4 solution. It would, therefore, seem plausible that one of the components of this universal buffer system has an undesirable effect on the behaviour of these electrodes.

Continuous titrations made using the universal buffer system suggested by Best and Samuel (50 cm^3) and sodium hydroxide (0.1 M) yield straight line plots. In this case, however, the electrodes were not permitted to equilibrate prior to titration and showed steps which corresponded to unbuffered zones on the pH scale

FIG 6·8

PLATED ELECTRODE [Rh on Pt] IN INDIVIDUAL SOLUTIONS



(see Chapter 3). The gradient, in this case, was super-Nernstian (-63 mV/pH), but this can be attributed to the effect of potential drift as can the steps observed in the unbuffered zones.

A further possible complication in a system such as this is introduced by the presence of dissolved oxygen. 'Stepwise' experiments in which U.B.4 was purged continuously with nitrogen gave low gradients at pH values above neutrality (-40 mV/pH for electrode E1 and -30 mV/pH for electrode E3) which increased to -90 mV/pH at pH values below pH 5. In this case, a negative potential drift was observable at all pH values.

A change of slope was also noticed when the solution was titrated continuously. It is, therefore, clear that the behaviour of the electrode potential with respect to pH is substantially altered by the presence or absence of dissolved oxygen. However, it would be imprudent, at this stage, to make any comments regarding the cause of these effects.

The remainder of this chapter has been directed towards the evaluation and interpretation of these and other possible sources of error.

6.1.5 Polarization Studies

When the e.m.f. of a galvanic cell is measured, it is important that no deviation from equilibrium conditions occurs. All instruments used in the measurement of e.m.f. require that a certain amount of current flows (Chapter 2). Even though this transfer of electricity may be infinitesimal, it follows

that the electrodes of a galvanic cell must act as working electrodes to some extent, and therefore must be capable of meeting these demands without significant disturbance of potential.[10]

In the last section, it was noted that rhodium electrodes prepared by plating gave a theoretical pH response when pH was changed continuously, but the potential - pH lines obtained from 'stepwise titrations' were less encouraging. This section is devoted to attempts at identifying the nature of this apparently faulty behaviour. Electrodes which meet the demands referred to in the first paragraph are good electrodes, and those that fail to do so are faulty. There are, of course, other reasons for defective electrode behaviour, and some of these are discussed in later sections.

Clearly, although the main interest of the investigation is not directed towards electrochemical kinetics, one would be extremely ill-advised to ignore kinetic aspects appertaining to any prospective pH electrode. However, in view of the limited time available, this investigation of kinetic behaviour has been restricted to a superficial examination of the behaviour of deposited electrodes in certain solutions exposed to atmospheric concentrations of oxygen.

Before attempting any assessment of the kinetic behaviour of a particular electrode, it is logical first to define the properties that are most desired. The ideal electrode would be a completely reversible, non-polarizable electrode, the potential of which is unaffected when current flows across the metal solution interface. This property would require the electrode to have

zero resistance or impedance. Since processes of chemical change and transport of matter must keep pace with the flow of current and do not occur in practice either unhindered or in the absence of a gradient of chemical potential, clearly the ideal non-polarizable electrode is unattainable. It is possible, however, that ideality may be approached under suitable conditions.[10]

It is possible to study the departure of any electrode from ideal reversibility on a quantitative basis. Every electrode at rest potential may be considered as a mobile equilibrium system, which is maintained by forward and back reactions proceeding at equal rates. The rates of the equilibria involved are then defined by the slowest step in the overall electrode process. Since all such processes involve the transfer of charge across the electrode-solution interface, their rates may be expressed in terms of electric currents. This is normally referred to as the exchange current and it is independent of any variation in the potential difference across the surface. For example, if the potential is biased in the negative direction, a finite cathodic current will flow. The net current is merely the difference between an increased forward reaction rate and a decreased back reaction rate.[10]

The Tafel relation:[10]

$$\eta = a + b \log i \qquad 6.5$$

is well established as the equation typical of the kinetics of the electrode processes under certain conditions (see below).

In this expression, η represents the overpotential (i.e. the difference between the potential when a current density (i) passes and the rest potential) and a and b are constants. The constant b is called the Tafel slope and this represents $-2.3\ RT\nu/\alpha nF$.[71] In this equation, n represents the number of electrons involved in the equilibrium, α and ν represent the transfer coefficient and the stoichiometric number respectively and R, T and F have the usual meanings (see Abbreviations). The above expression may be derived from a kinetic point of view but this would be outside the scope of this account.

If the reaction is mass transport controlled the following equation is applicable:

$$E = E^{o'} + 2.3\frac{RT}{nF}\log\frac{\gamma_{red}}{\gamma_{ox}} + 2.3\frac{RT}{nF}\log\frac{i_d - i}{i} \qquad 6.5a$$

where E is the electrode potential, $E^{o'}$ is the apparent standard electrode potential, i_d is the limiting diffusion current density and γ_{red} and γ_{ox} are diffusion current coefficients and are functions of the rate of stirring.[71]

Equation 6.5 relates solely to the separate current densities associated with the individual processes referred to above. It will, therefore, only hold for experimentally observed currents at potentials sufficiently distant from the rest potential to ensure that one of the opposing currents is suppressed. Near equilibrium (less than 10 mV), the Tafel relation becomes:

$$i = i_o\, n\eta F / RT \qquad 6.6$$

because of the joint effect of the Tafel laws for the opposing currents.[10,71] In the above expression i_o signifies the exchange current density.

It can be seen from equation 6.6 that, if i is constant, in order to obtain small overpotential, i_o must be large. Clearly, this condition is unattainable since the exchange

current density would have to tend to infinity. In practice, however, it is sufficient for the exchange current to be large in comparison to the net current it is likely to pass in use. If, for any reason, the exchange current should fall too low, the electrode might, not only, become polarizable, but also, other processes capable of sustaining a higher i_o may take over. As was indicated in Chapter 1, in the presence of impurities such as oxygen the maintenance of this condition may be crucial.[10]

The exchange currents densities produced at metal-solution interfaces have been given by Ives and Janz[10] as varying from about 10^{-2} to 10^{-10} amp.cm^{-2}. In order to be useful for pH measurement or for reference purposes, however, the electrode selected would have to have a value of i_o on a much more restricted range than this. It would be well outside the terms of reference of this investigation to attempt precise measurements of exchange current. However, an indirect indication of whether or not an electrode has a sufficiently large i_o value may be obtained from micropolarization tests[10] such as those described below.

As can be seen from equation 6.6, in the vicinity of the rest potential, net current passed varies linearly with the displacement of potential from the equilibrium value. The slope of such a plot would then be directly proportional to the exchange current. Clearly, the greater the slope obtained, the more reversible an electrode may be considered. Any hysteresis observed indicates gross irreversibility.[10]

Simple micropolarization tests can be easily carried out

using a potentiometer and a D.V.M. set up in parallel to a resistance so that it behaves as a galvanometer. Using this apparatus, the potential can be displaced by increments of 1 mV and the corresponding values of current and potential then plotted as previously described. It was found that when this technique was applied to electrode G1, although the indicated current altered by 0.6 to 0.7 μA when the potential was displaced by increments of 1 mV (up to 3 mV), this value quickly fell back to zero on standing for 2 to 5 minutes. Similarly, currents of 0.7 to 0.9 μA were observed in the case of electrode G4 and these fell to zero within 7 minutes. In both cases, a neutralized U.B.4 solution was employed.

As a result of these measurements, it was decided to replace the potentiometer with a potentiostat (Chemical Electronics Type TR70-2A). The potential was held at a fixed value rather than 'backed off'. It was found that, when electrode G4 was subjected to this treatment, maximum currents of 0.9 to 1.0 μA per 1 mV increment were observed, but these, once again, fell to zero ($\pm$ 0.02 mV) within 5 to 10 minutes. In this experiment a phosphate solution (pH 6.99, see Chapter 2) was employed.

The fact that a current does flow when the applied potential is displaced from the rest potential suggests that the electrode does possess a certain degree of reversibility but the rapid drift back to zero current is more difficult to explain.

In view of the difficulties encountered in micropolarization tests, it was decided to extend the study of the polarizability of these electrodes to other methods involving more specialized equipment. The apparatus was basically the same as that described

in section 6.1.2 (fig. 6.1) except that the chart recorder was replaced by a storage oscilloscope (Tektronics 5103N). The remainder of the apparatus consisted of a potentiostat (Chemical Electronics Type 703A) and a pulse generator (constructed in the School of Chemistry). The photographs shown in this section were taken from the oscilloscope using a Polaroid Land Camera. In this account these are shown as figures traced from the photographs.

In this portion of the work, two solutions have been used, both of which were referred to in Chapter 3 and in both cases, the solutions were exposed to an oxygen/nitrogen mixture in 'artificial air' proportions. In order to establish whether the electrode processes were affected by the pH of the solution, experiments were carried out, both in U.B.4 (pH 10.4) and in a phosphate mixture (pH 6.99). If this was the case, it might account for the sigmoid character of the potential - pH curve observed, after a period of time, (see section 6.1.4). Atmospheric conditions were chosen as these were most often encountered in other experiments and it was under these conditions that the perplexing sigmoid response was observed.

The pyrex glass cell used for these experiments, was identical with that used for the 'oxygen response' experiments. Clearly a cell designed to eliminate ohmic potential drop would be preferable but it was decided that the limited nature of this section of the work did not warrant the expense involved and extra time consumed in the construction of a more complicated cell. Instead, it was decided to use an A.C. measurement technique employing an 'S.E. Laboratories Transfer Function Analyzer SM 272' to determine

the resistance and then compensate for the ohmic drop. In order to complete a three electrode system, a calomel reference electrode and a platinum foil counter electrode (0.5 cm x 1.5 cm) were introduced into the solution.

Having set up the apparatus and switched in the potentiostat at the relevant rest potential, electrodes G1 and G4 were first examined by applying a single 'square' pulse to each electrode. Figure 6.9 shows the current-time behaviour of electrode G1 after a 9 mV anodic pulse 32 ms duration has been applied to the electrode immersed in the phosphate buffer solution. Figure 6.10, on the other hand, shows a 10 mV anodic pulse of the same duration applied to electrode G4. It can be seen that, after rapidly rising at the beginning of the pulse, the current falls more slowly, levelling off as it does so. This indicates that the process is mass transfer controlled in both cases but it would appear that the electrodes are not completely mass transfer controlled since the current does not level off immediately. The current-time transient which levels off first is the best mass transfer controlled system. The 'mirror images' observed on Fig. 6.9 and Fig. 6.10 also show that the process is mass transfer controlled. The X and Y scales in these figures are 10 ms/div and 50 μA/div. respectively.

When pulses of 10 mV were applied to the same electrodes, immersed in U.B.4, similar traces were observed on the oscilloscope. In both cases, the recovery characteristics for this solution seem to suggest that the process tends towards being charge transfer controlled. Fig. 6.11 shows the trace obtained using electrode G1. The traces obtained using cathodic pulses (not illustrated) were almost identical to those described above.

FIGURE 6.9

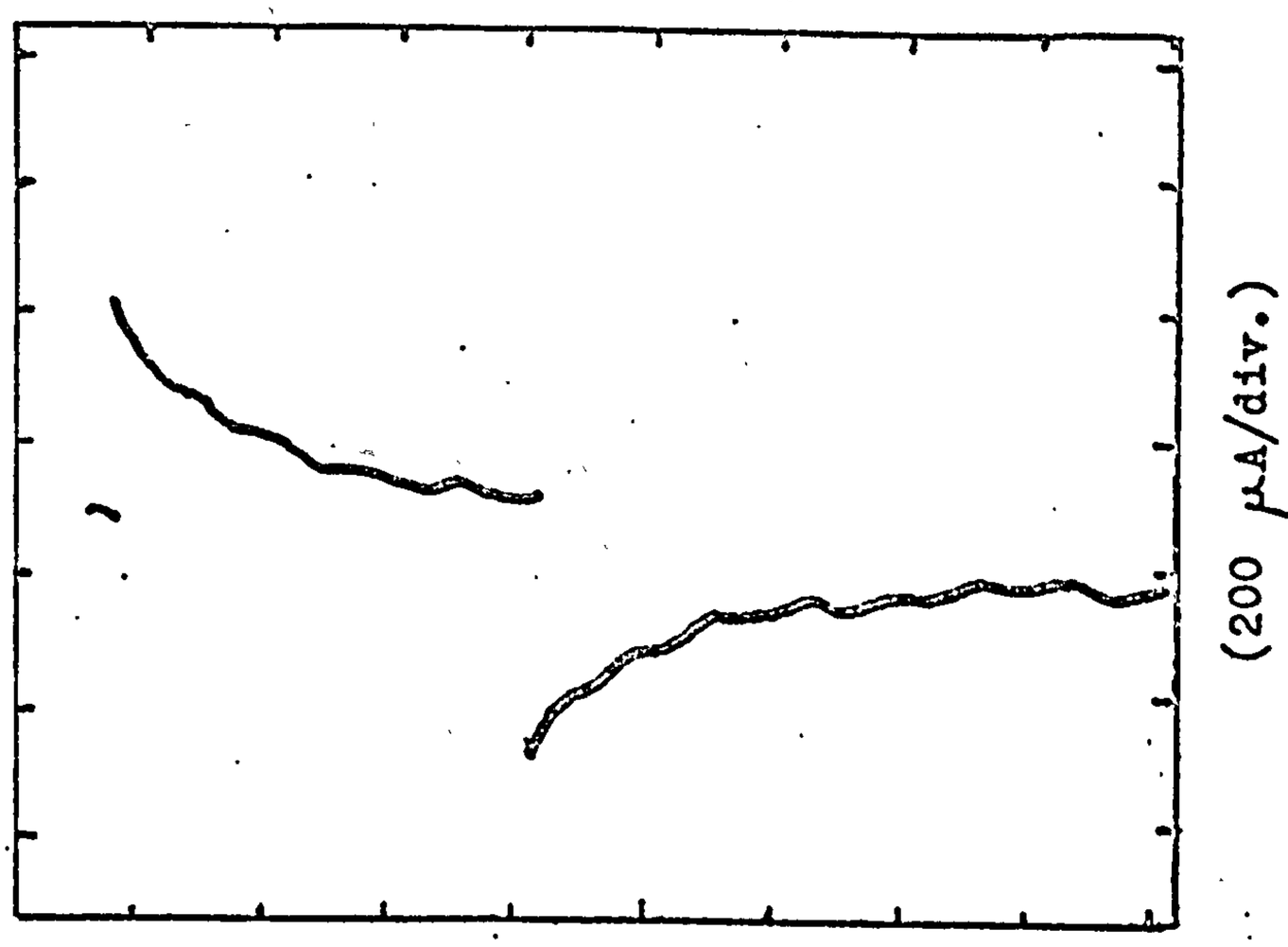


FIGURE 6.10

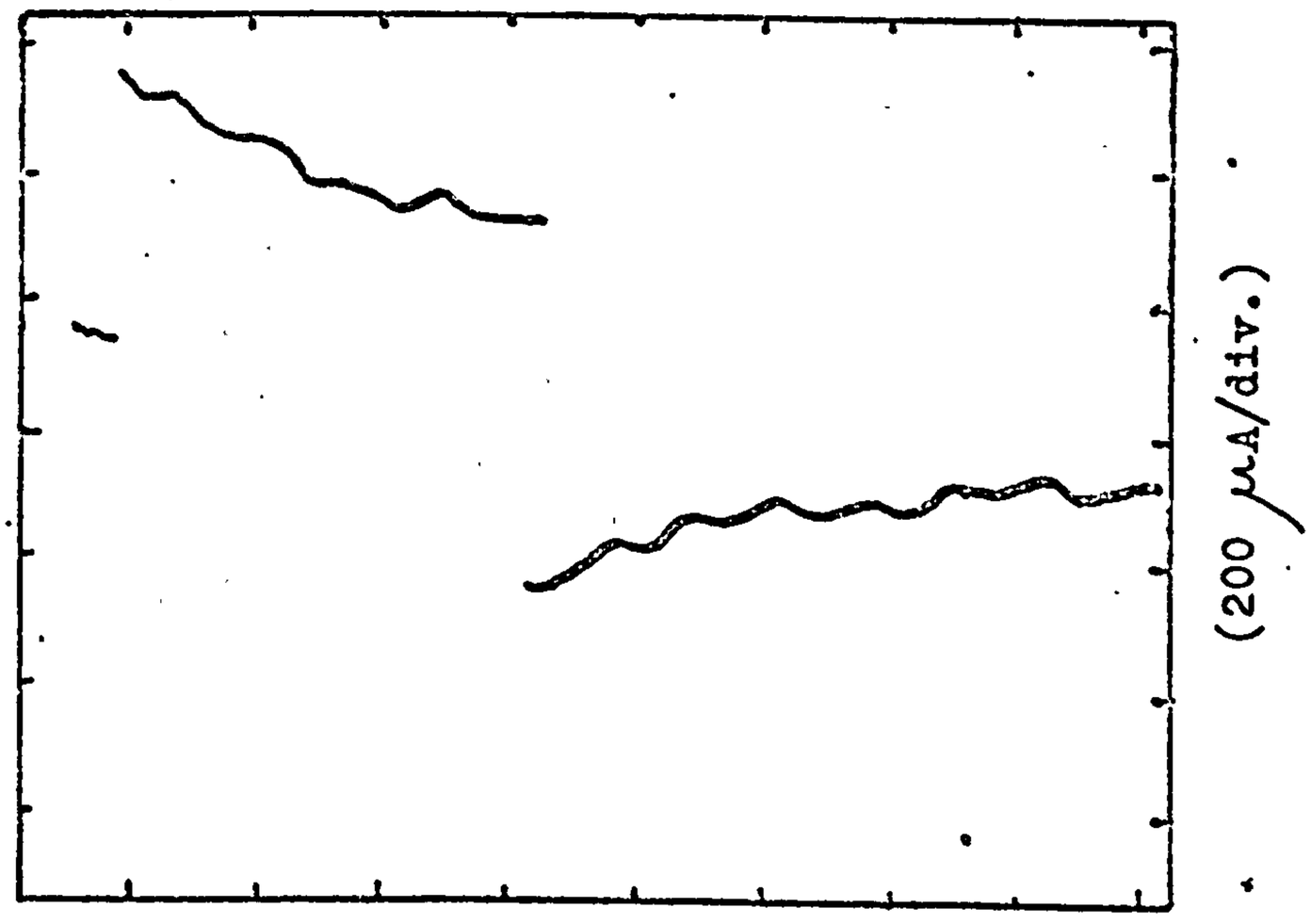


FIGURE 6.11

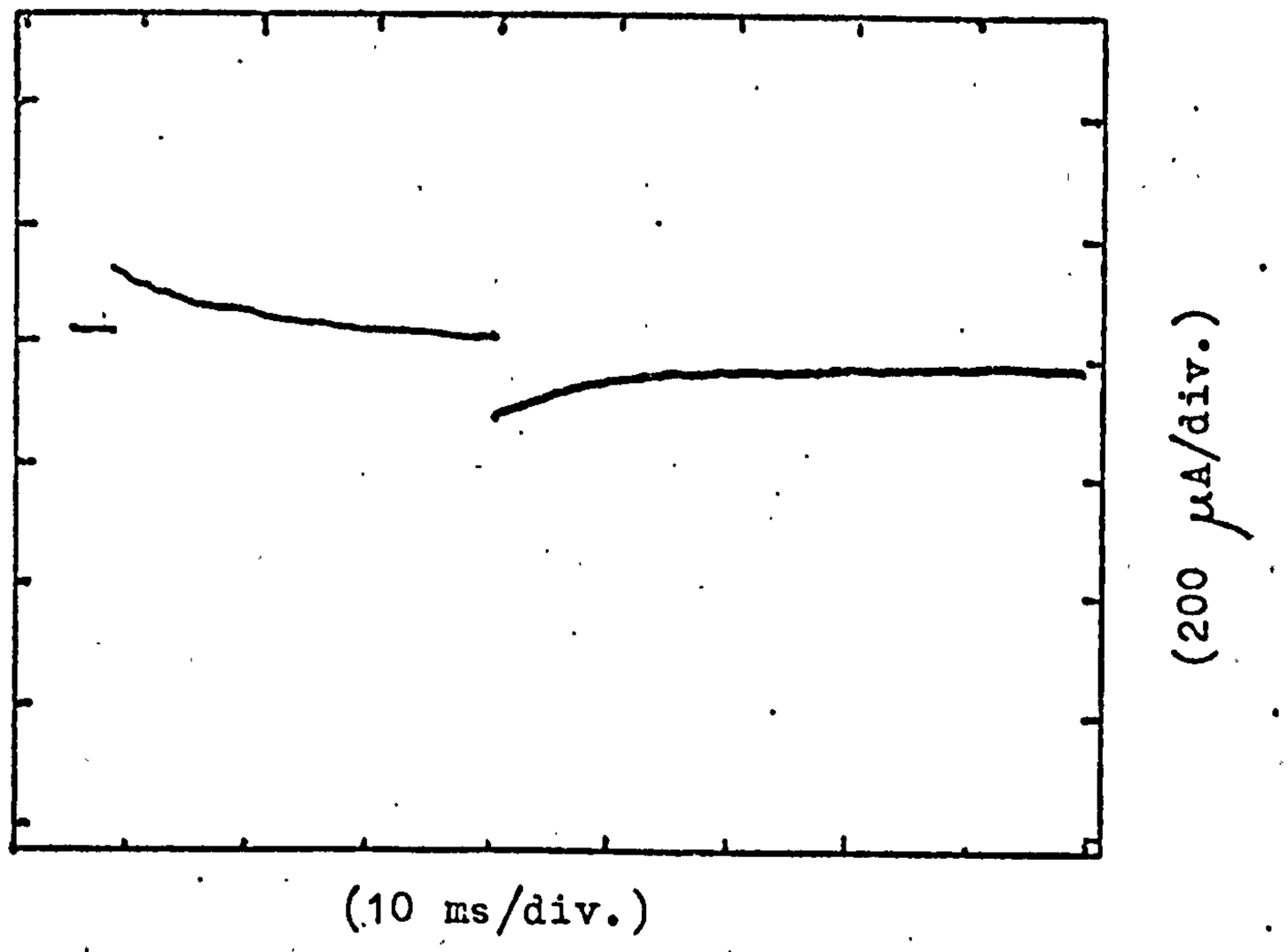
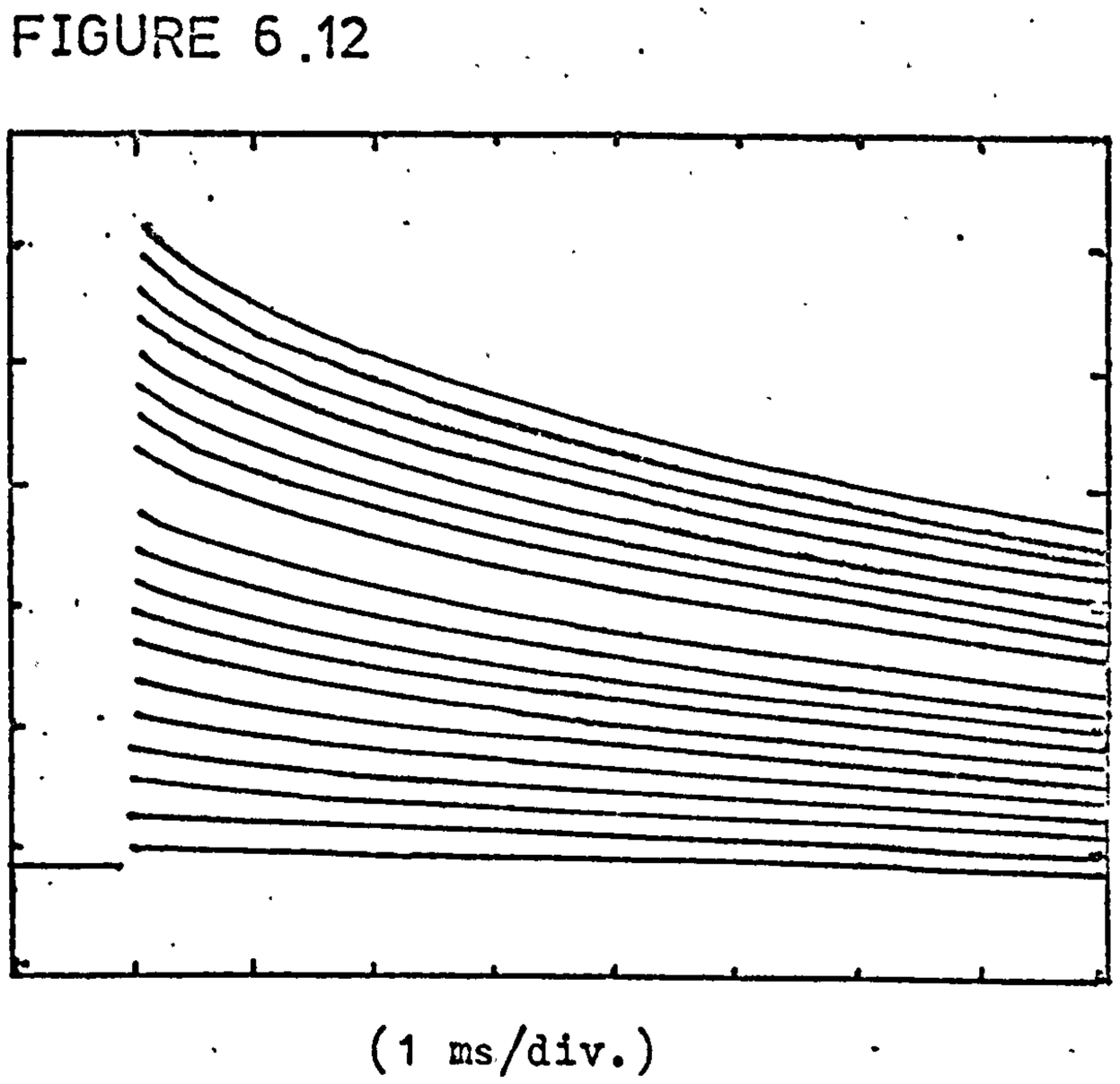


FIGURE 6.12



Having established that these electrodes do appear to be mass transfer controlled to a certain extent, it was decided to extend this investigation to obtain 'families' of traces by applying a series of incremental single, short pulses to the electrode concerned. The duration of each pulse was reduced to 10 ms and the X and Y scales were set at 1 ms per division and 200 μA per division respectively. Figs. 6.12 and 6.13 show the effect of applying a series of anodic pulses, (increased by increments of 5 mV), to electrode G4. Fig. 6.14 shows the effect of similar cathodic pulses when applied to electrode G4. Finally, Figs. 6.15 and 6.16 show the traces obtained when a series of anodic and cathodic pulses, respectively, (increments of 10 mV) were applied to electrode G4 immersed in U.B.4. (The Y axis scale was increased to 100 μA per division.) Similar traces were obtained for electrode G1 (not illustrated).

The value of obtaining 'families' of traces such as these lies in the fact, that, if currents are taken after a fixed period of time, Tafel plots can be obtained by plotting the log of current against the applied potential. All currents values were taken after 4 ms. Since no precautions were taken to eliminate ohmic potential drop, before Tafel plots could be made it was first necessary to determine the resistance of the cell. When subjected to phosphate solution, electrode G1 was found to have a resistance of 87.7 Ω, while electrode G4 was found to have a resistance of 53.6 Ω. These resistance values were considered to be excessive, consequently the cell was modified slightly before investigating the behaviour of the electrodes in U.B.4 solution. There electrodes G1 and G4 were found to have resistances of 30.6 Ω

FIG. 6.13

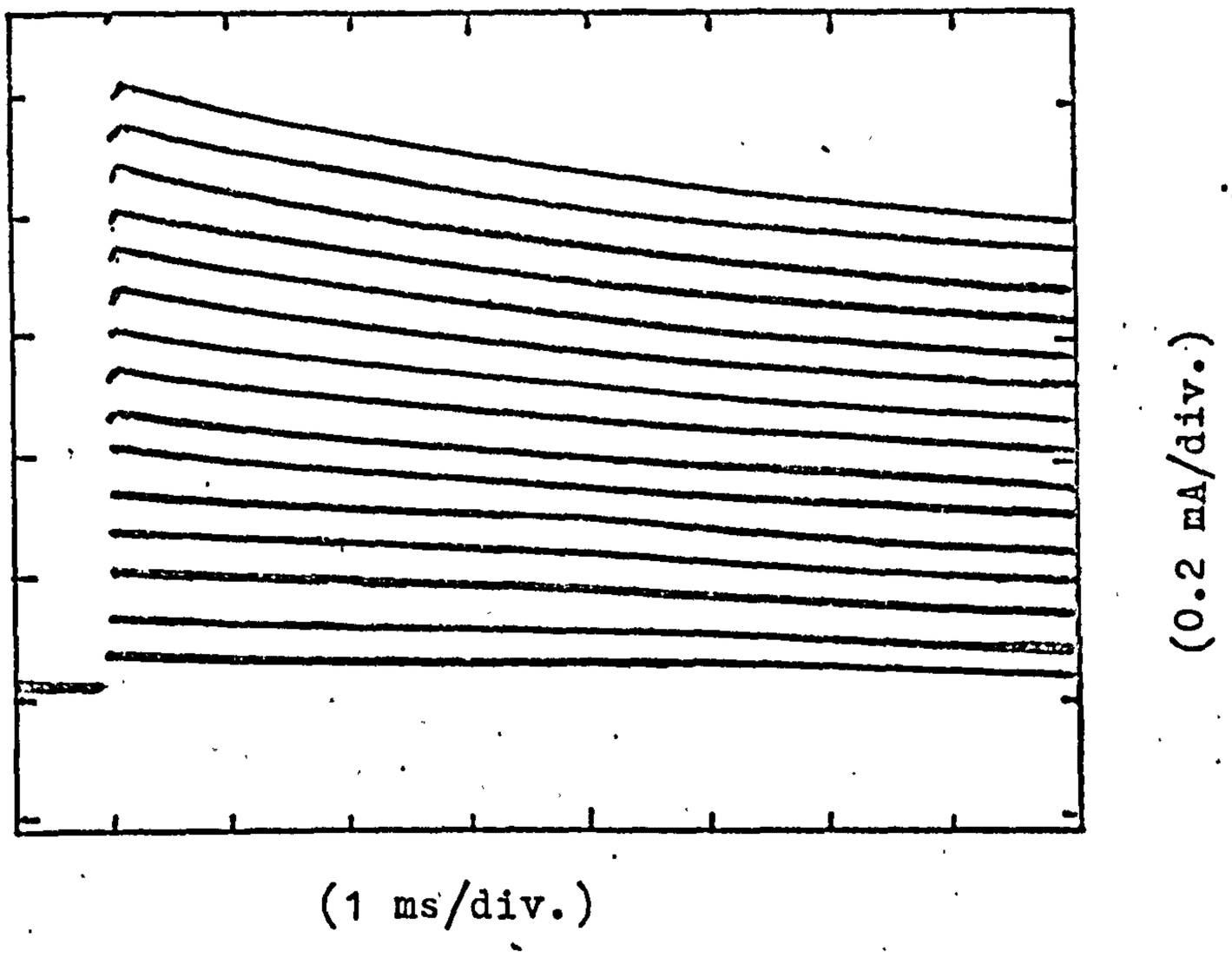


FIG. 6.14

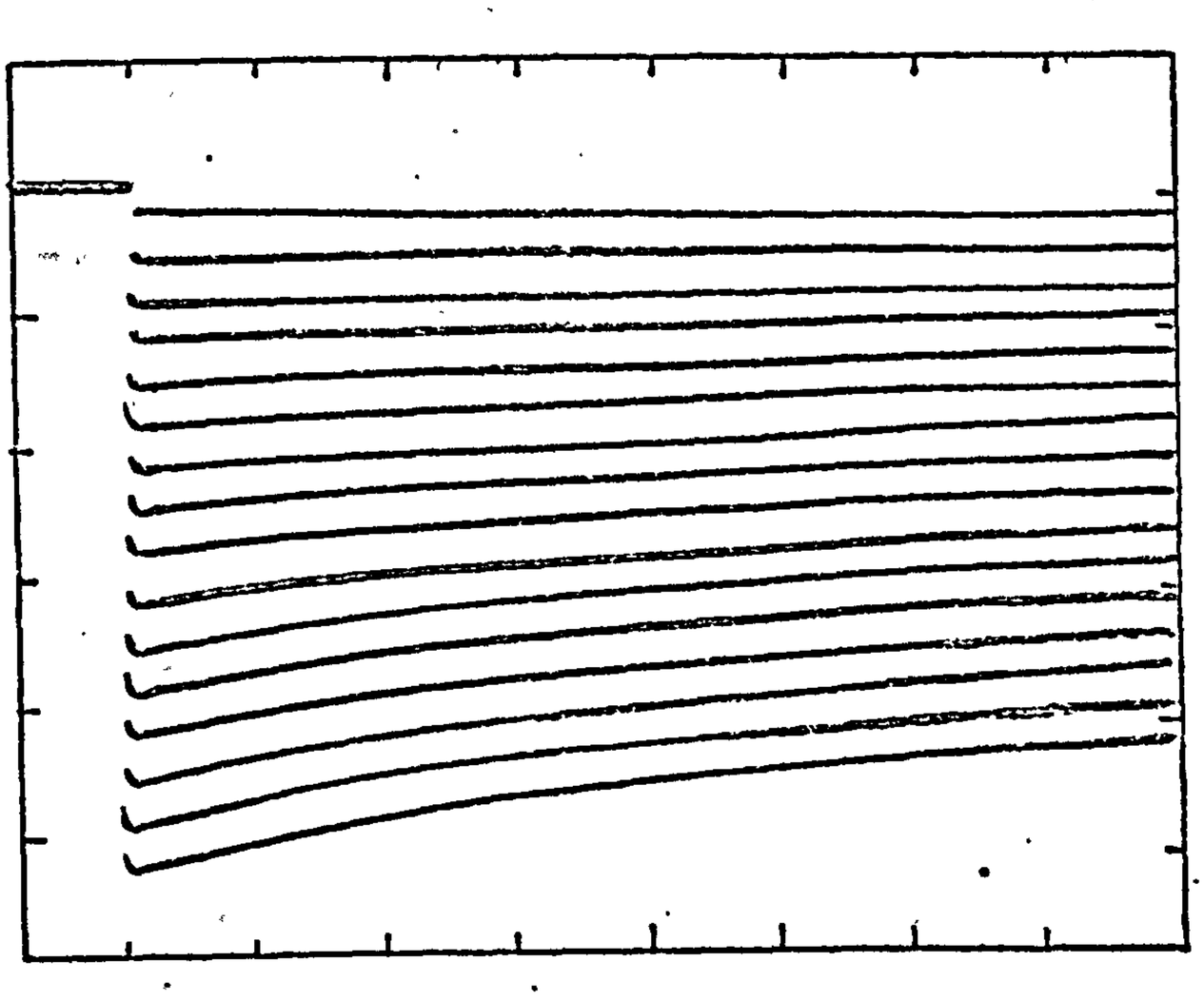


FIG. 6.15

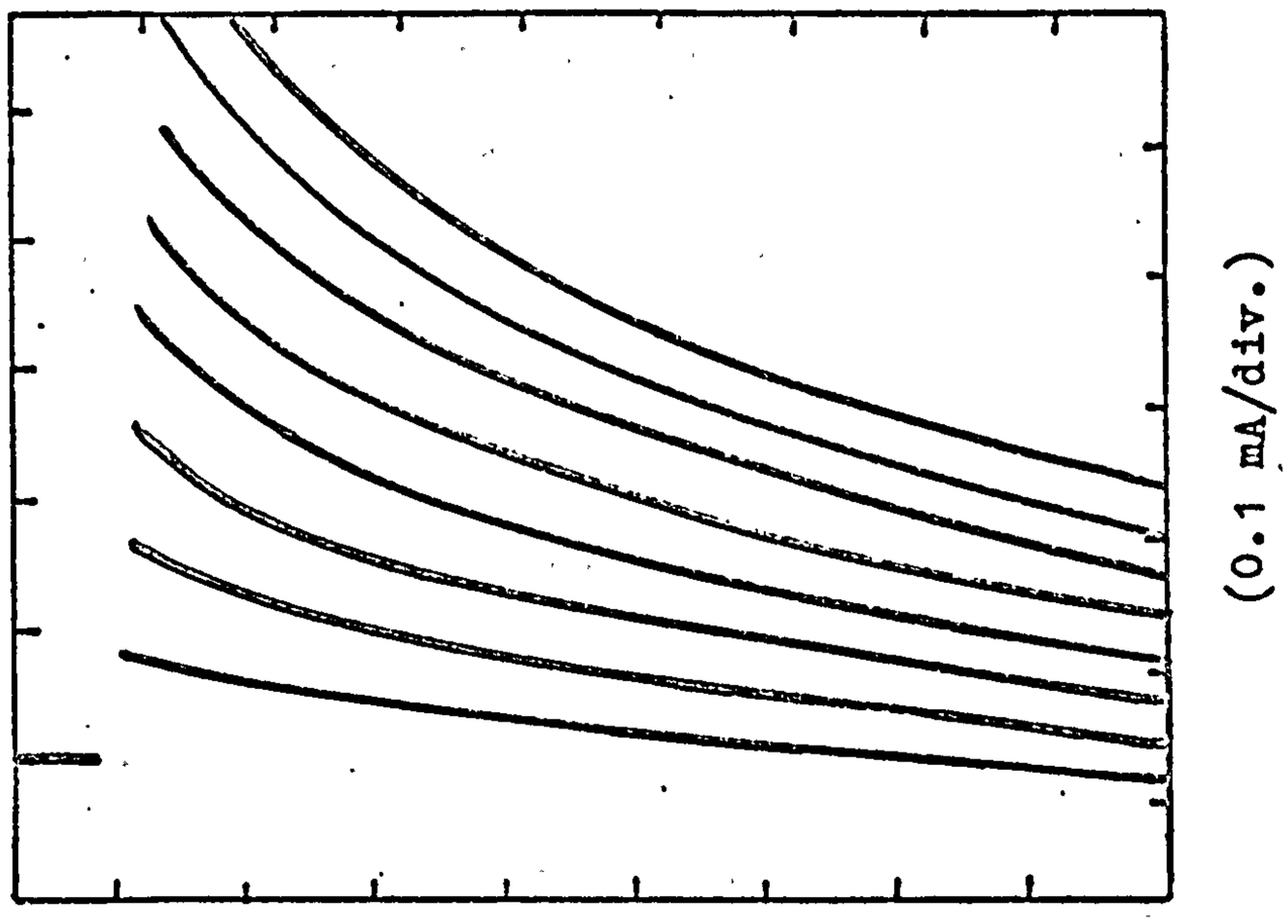
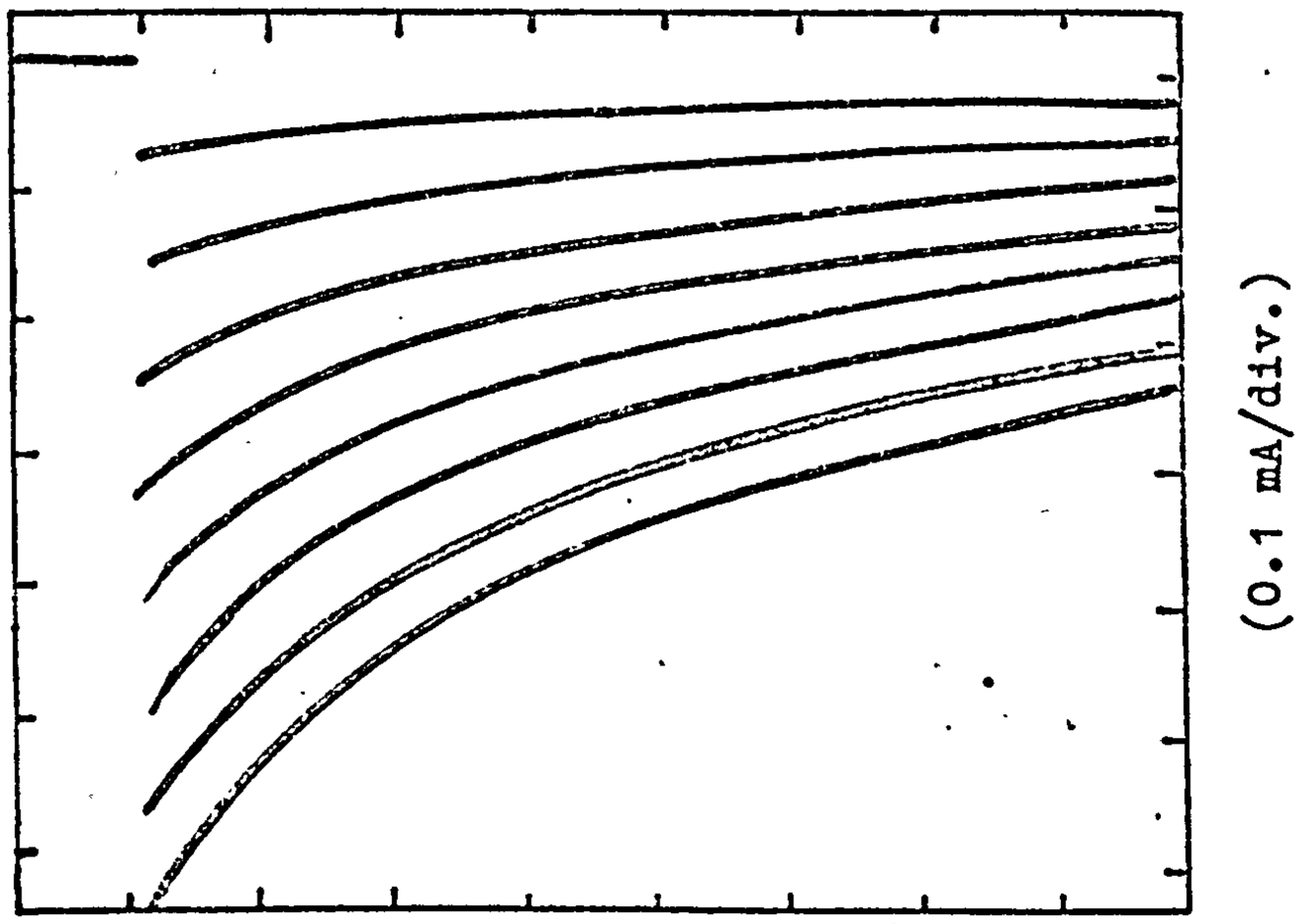


FIG. 6.16



and 22.2 Ω respectively. Figures 6.17 and 6.18 show the Tafel relationships obtained after subtracting the ohmic drop from the applied potential.

Since applying such an ohmic correction to the potential inevitably results in the points being compressed on the plotted graph, it is not surprising that a Tafel slope is more easily discerned for the plots obtained from the phosphate solution. For the plots obtained from the U.B.4 solution, the smaller ohmic corrections and the fact that 10 mV increments were used, result in widely spaced points on the Tafel plots. The latter condition was necessary because the traces obtained on the oscilloscope tended to merge when 5 mV increments were used.

Although plots obtained for both electrodes in neutral solution do show some discrepancy, it is clear that a Tafel slope of 30 mV per decade is applicable between potentials of 10 and 20 mV. Few points are available between 0 and 10 mV and those obtained seem to indicate that the process is convection controlled in this region.[73] At potentials above 20 mV, it appears that the current becomes diffusion limited. To a lesser extent, the current is also still affected by the resistance of the solution.

For the reasons mentioned above, it is more difficult to fit a Tafel slope to the plot obtained from alkaline solutions, however, between 10 to 20 mV the same condition applies, i.e. a slope of 30 mV per decade. The implications of these observations will be discussed at the end of this section.

Since the exchange current (I_o) is the current flowing in both directions at the rest potential (E_e), it is clear that if

FIG. 6·17

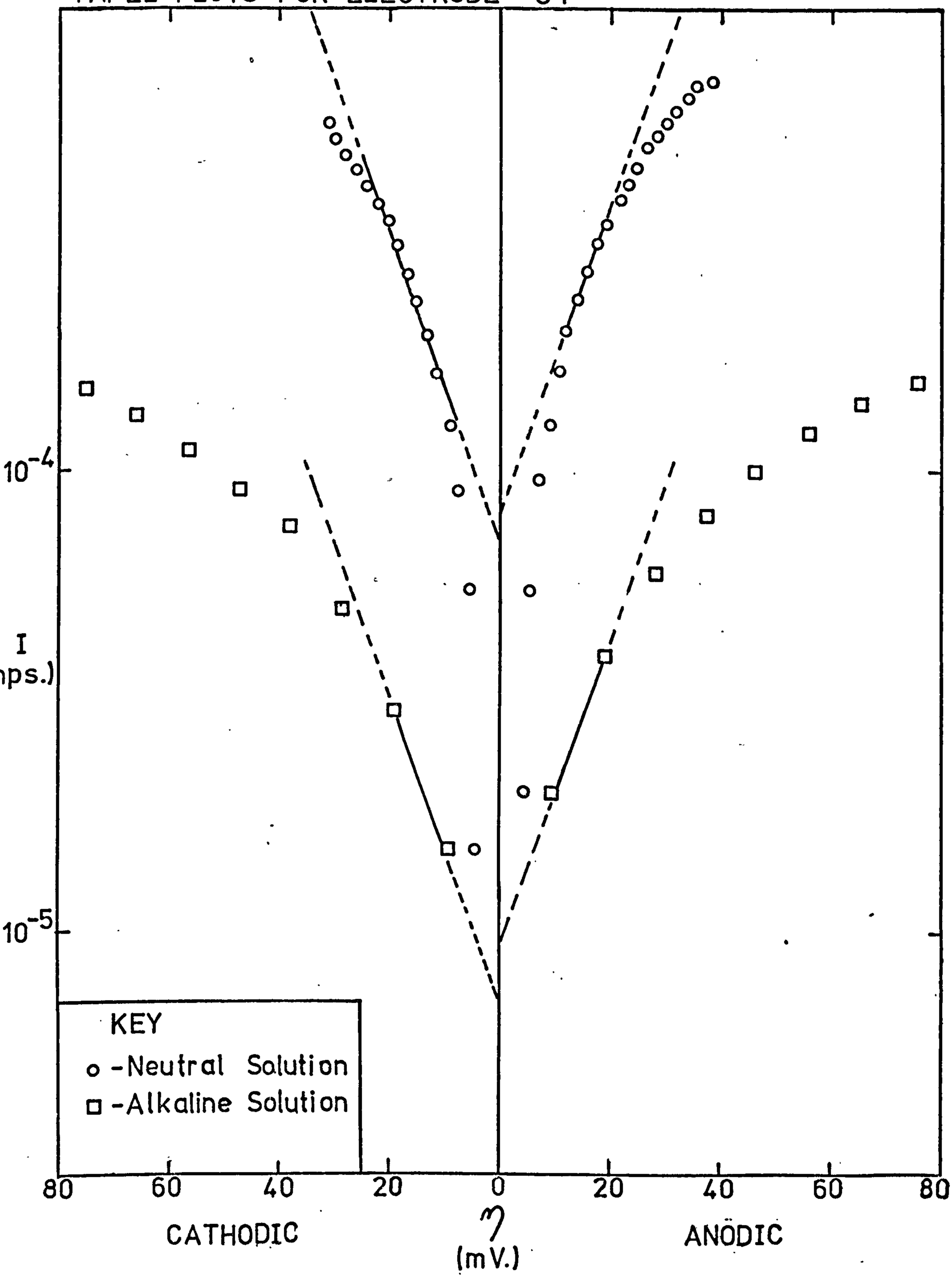
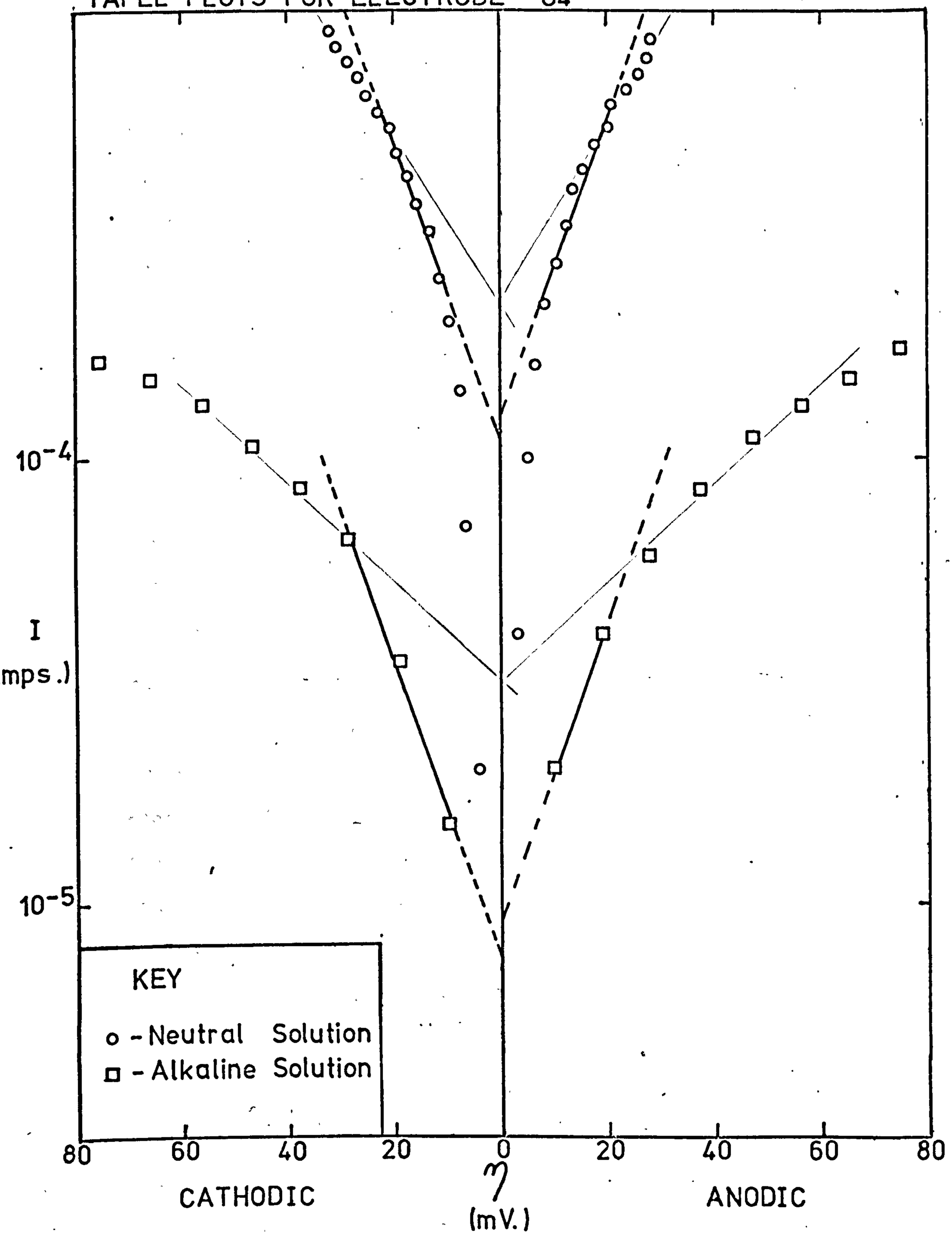

TAFEL PLOTS FOR ELECTRODE G1
10^{-4}
10^{-5}
I
(Amps.)
KEY
o -Neutral Solution
□ -Alkaline Solution
80
60
40
20
0
20
40
60
80
CATHODIC
η
(mV.)
ANODIC

FIG. 6·18

TAFEL PLOTS FOR ELECTRODE G4



these lines are extrapolated to zero overpotential, an estimate of the exchange current may be obtained. Therefore, it appears that electrodes G1 and G4 have approximate I_o values of 1.2×10^{-4} A and 7×10^{-5} A respectively in neutral solution and 7.5 to 9×10^{-6} A and 7 to 9.5×10^{-6} A in alkaline solution. Current density is defined as the current divided by the geometrical area of the electrode,[72] i.e. the macroscopic area. It should, therefore, be a simple matter to convert these approximate exchange current values to approximate exchange current densities, (i_o). Measurements taken with a micrometer screw gauge indicate that the geometrical surface areas of electrodes G1 and G4 are, respectively, 0.1558 cm^2 and 0.2345 cm^2. The approximate exchange current densities for electrodes G1 and G4 in neutral solution can now be calculated to be 7.7×10^{-4} A cm^{-2} and 3.0×10^{-4} A cm^{-2} respectively.

To conclude this section of the investigation, a number of rapid linear potential sweeps were carried out using these electrodes. Figs. 6.19 and 6.20 show anodic current-potential traces obtained from potential sweeps from E_e to 100 mV, for electrodes G1 and G4, respectively, in phosphate solution. Figs. 6.21 and 6.22 show the effect of similar cathodic sweeps. The sweep rates used were 1 V s^{-1}, 100 mV s^{-1} and 10 V s^{-1}. In each figure the x scale is 20 mV per division. The y scale is 0.2 mA per division, for figs. 6.19 and 6.20 and 0.1 mA per division, for figs. 6.21 and 6.22.

It can be seen from these figures that the shape of the current-potential curves obtained and the maximum current flowing are both dependent on the sweep rates employed. The larger hysteresis effects correspond to the faster sweep rates. This

FIGURE 6.19

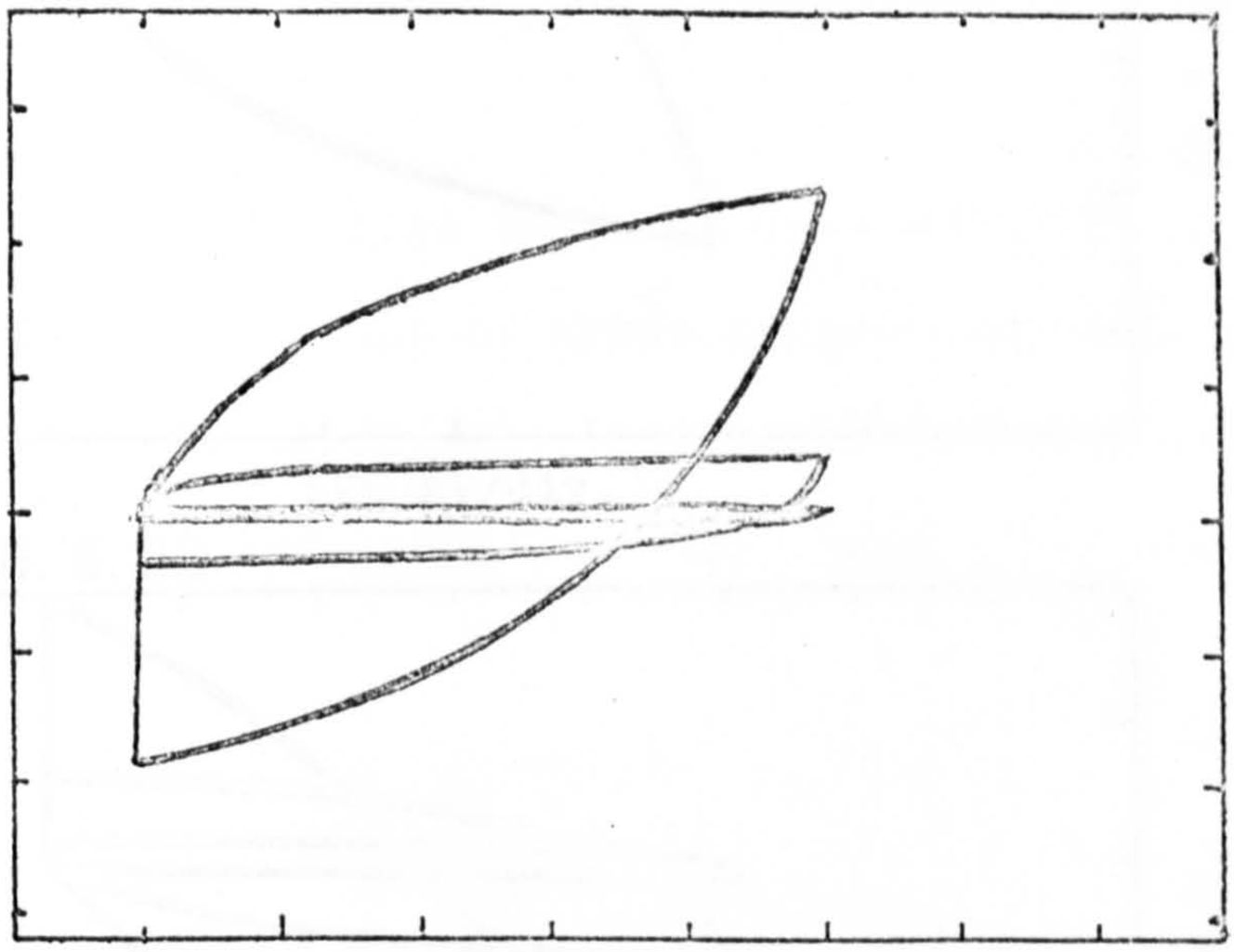


FIGURE 6.20

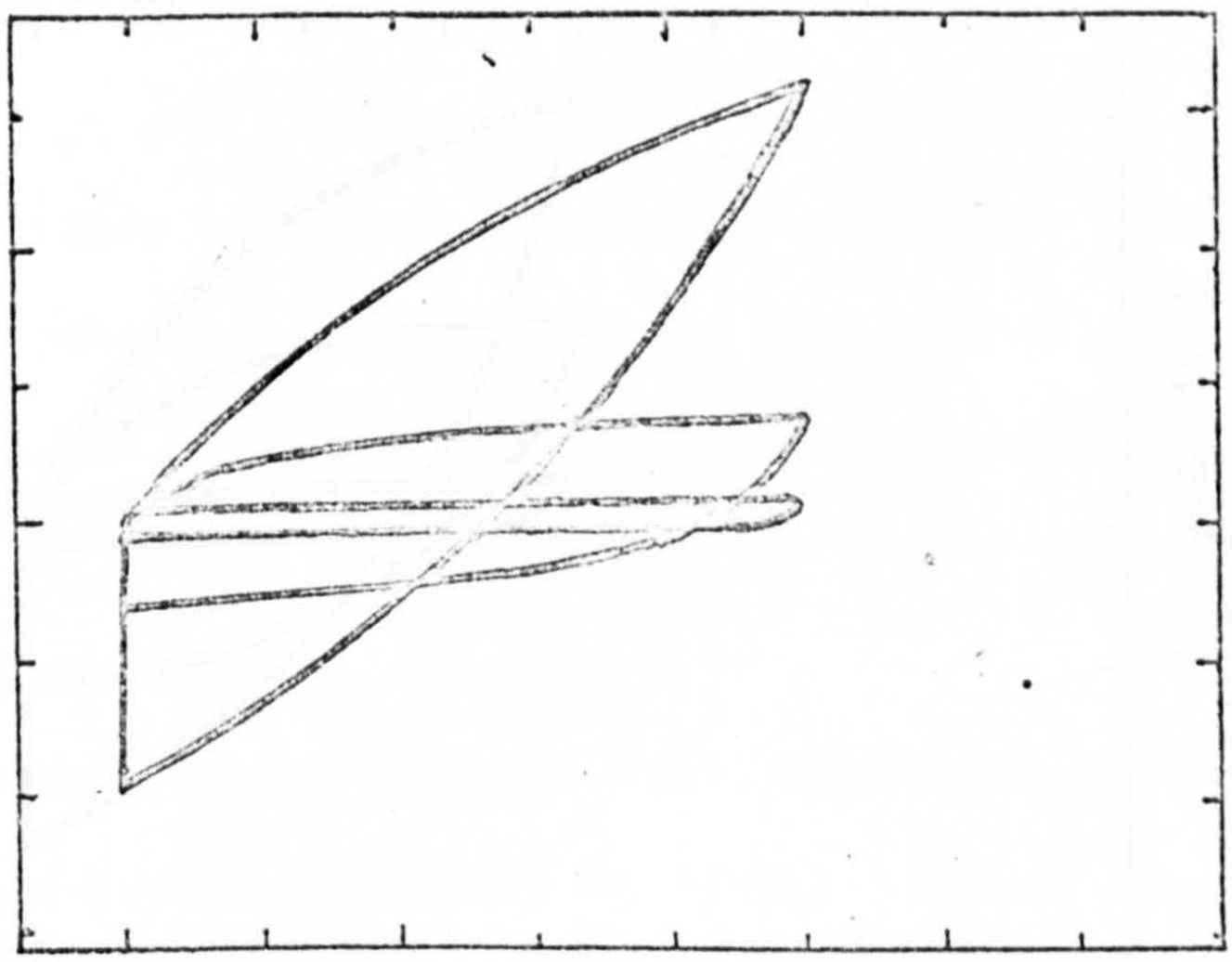


FIG. 6.21

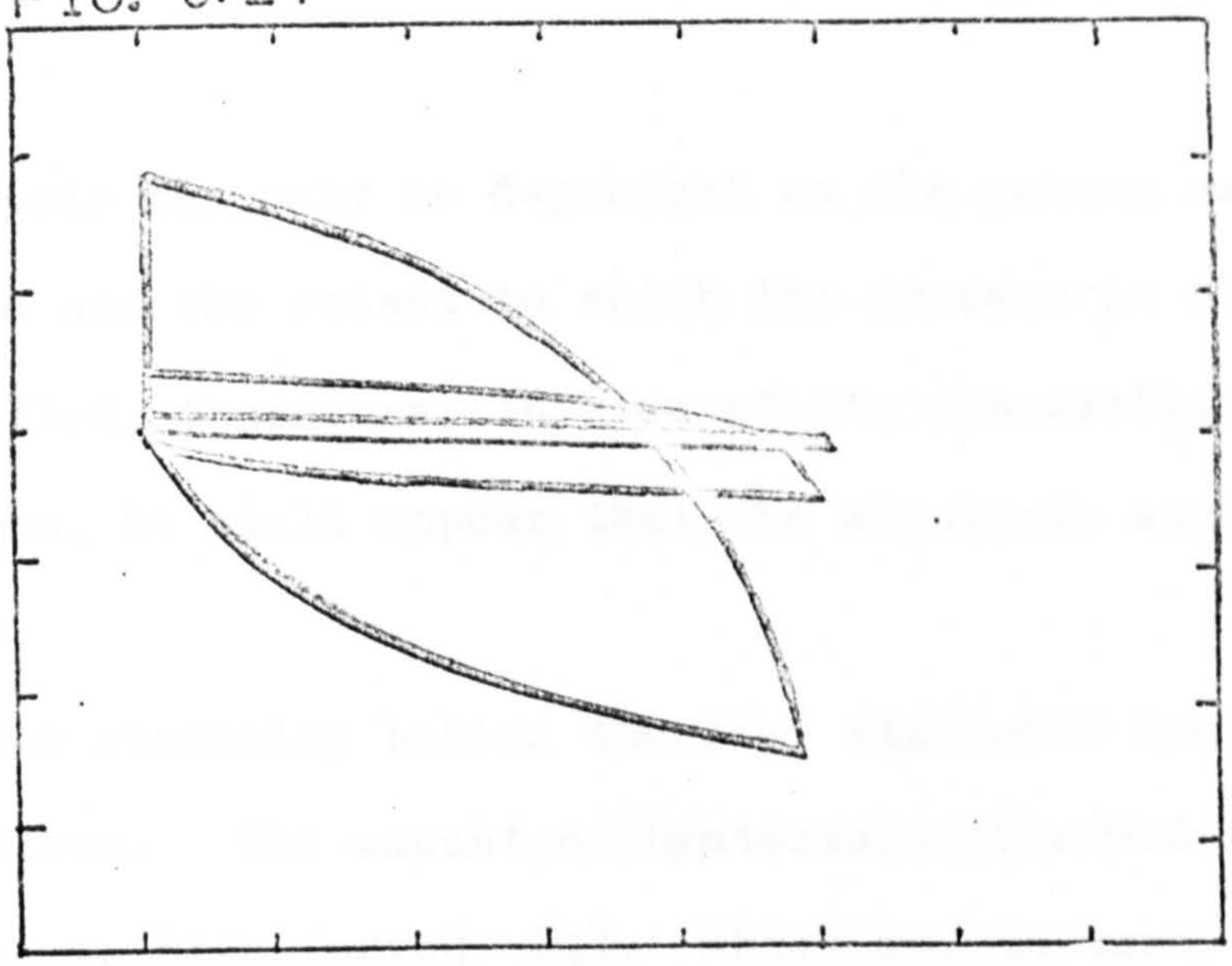


FIG. 6.22

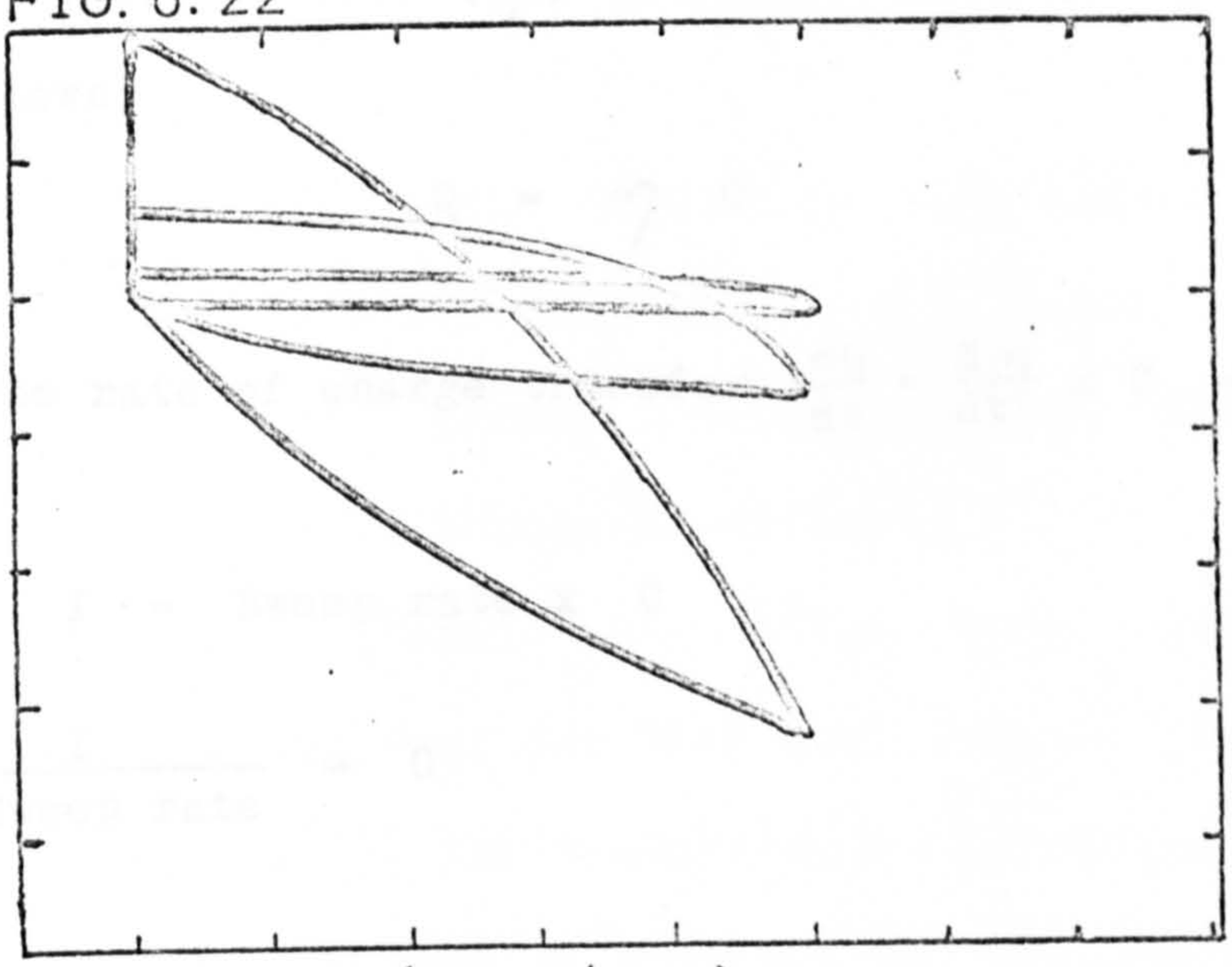
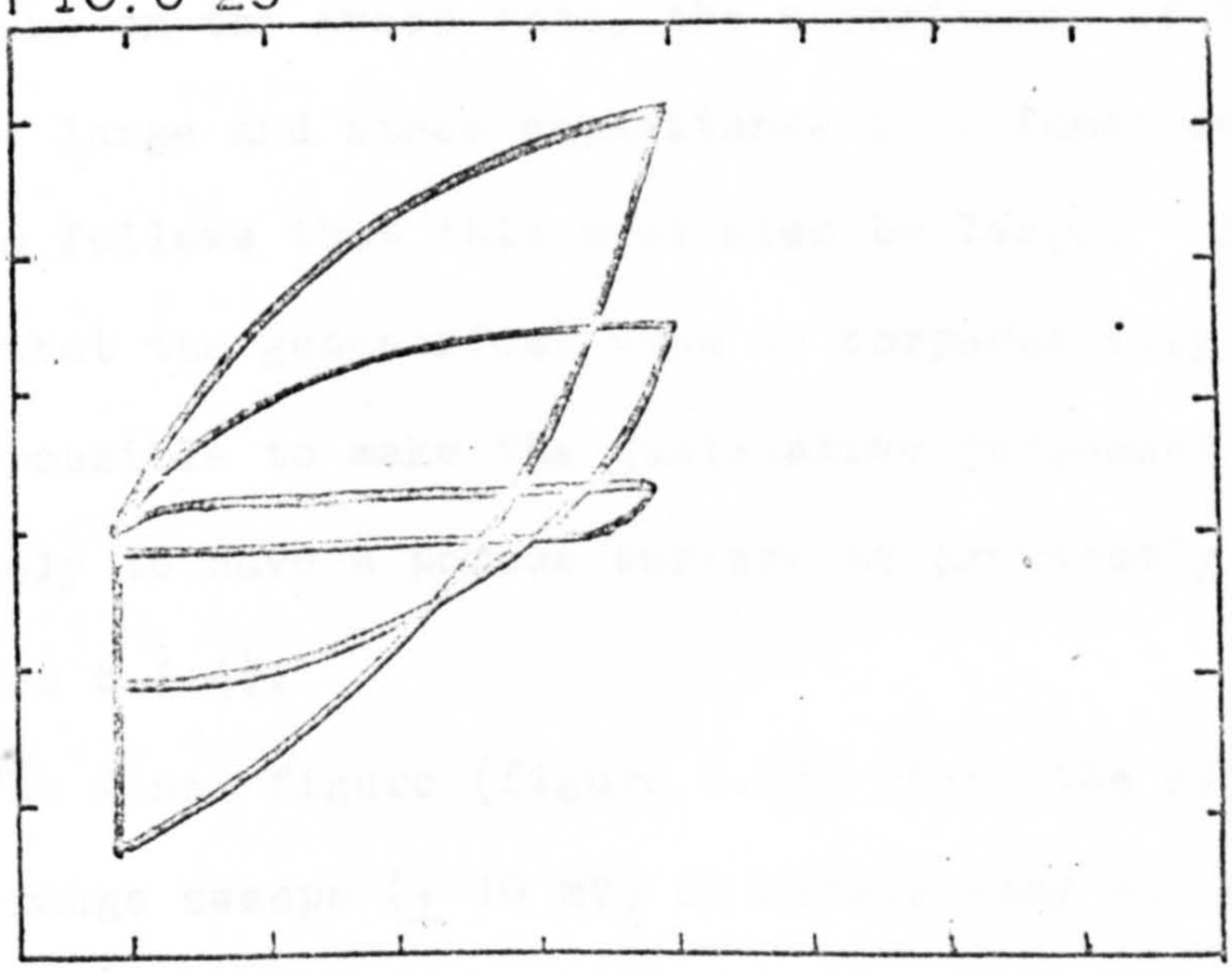


FIG. 6 23



hysteresis can only be dependent on the porous nature of the surface and the extent to which the process is charge transfer controlled, therefore, in view of the observations made in other sections, it would appear that the electrode surface is extremely porous.

The reasoning behind the last statement can be explained as follows. The amount of hysteresis observed is related to the charge transferred (Q), which is, in turn, proportional to the overpotential (η) and the capacity of the electrode (C) as follows:

$$Q = \eta \; C \qquad 6.7$$

$$\therefore \text{ The rate of charge transfer } \frac{dQ}{dt} = \frac{d\eta}{dt} \times C = I \qquad 6.8$$

$$\therefore \quad I = \text{Sweep rate} \times C \qquad 6.9$$

$$\text{or} \quad \frac{I}{\text{Sweep rate}} = C \qquad 6.10$$

Therefore, it follows that, if the current flowing is dependent on the sweep rate, the capacitance of the electrode must be large and since capacitance is a function of real area, it also follows that this must also be large. It has already been shown that the geometrical area is comparatively small, therefore, it is possible to make the qualitative judgement that the electrode is likely to have a porous surface as previously suggested (section 6.1.4).

The final figure (figure 6.23) shows the effect of rapid short range sweeps ($\pm$ 10 mV) on either side of the rest potential

(electrode G1). The sweep rates employed were 320 mV s^{-1}, 100 mV s^{-1} and 10 mV s^{-1}, while the x and y scales were 5 mV per division and 20 μA per division respectively. The conclusions that may be drawn from this experiment are identical to those given above.

It is useful at this point to summarize the conclusions drawn in this section most of which are essentially qualitative in nature. Micropolarization tests show that a current is passed when the applied potential is displaced from E_e but this rapidly falls to zero.

It is clear that the process is mass transfer controlled to a certain extent i.e. the reaction is fairly fast, but not infinitely fast.[73] Linear potential sweeps indicate that the electrode surface is porous as expected.

After applying ohmic corrections, Tafel slopes of 30 mV per decade are obtained for both electródes. From the Tafel relation (eq. 6.5), the process under investigation involves the transfer of 2 electrons in the rate determining step rather than 1 electron as pH measurements which are relatively slow seem to indicate (section 6.1.4). It is clear, therefore, that the rest potential of the electrode is not controlled by a single process as desired but, in fact, two or more processes must take place. It is conceivable that the process monitored by these measurements may be that of oxide formation, although it is difficult to see what oxide formation process could be responsible for a 2 electron process. One possibility is given below:

$$Rh \xrightarrow{\text{slowest step}} Rh^{2+} + 2e \qquad 6.11$$

(the Rh^{2+} would then be attacked by OH^-)

Since O_2 is electrochemically active this may also be involved.

Such a process, however, would cause a potential drift in the positive direction[73] and this could be responsible for the sigmoid pH response obtained from the long term experiments referred to previously.

Finally, the approximate exchange current densities deduced from these experiments are in the upper region of the range, 10^{-2} to 10^{-10} A per cm^2, quoted by Ives and Janz[10] for reference electrodes. It is perhaps significant that the i_o values obtained from alkaline solution show an approximately ten fold decrease on the values obtained from neutral solutions and would therefore become more polarizable and susceptible to interference by other reactions as shown previously. It must be pointed out, however, that this decrease could be due to the deterioration of the electrodes and not the change in environment.

6.2 Electrode Behaviour Over a Period of Time and Reproducibility

It has been shown in previous chapters that metal-metal-oxide electrodes tend to suffer from drifts in potential. The electrode system described in this chapter is no exception to this general rule. In fact, of all the electrodes examined in this work, only the antimony electrode was found to be free from pronounced potential drifts.

Two kinds of potential drifts were encountered, those observed after the pH of a particular solution has been altered and those which take place when an electrode has been removed from a particular solution and replaced in another. Potential drifts of the latter category are referred to in this investigation by the term, 'Initial Transients'.

The other sort of potential drift was confined to measurements made using universal buffer solutions. These drifts are not reproducible between experiments, but a few general points can be noted. Electrodes exposed to U.B.4 show least tendency to drift between pH 5 and 6. At some point between these pH values a reversal of the direction of drift takes place. It is reasonable to assume that this phenomenon is associated with a change of process or a reversal in direction of a particular process.

For electrodes deposited at -400 mV with respect to the S.C.E., potentials measured at pH values above those given in the previous paragraph, show positive overall drifts, while those measured under more acid conditions, show negative drifts. Below approximately pH 3, the direction is once again reversed. Electrodes prepared at higher deposition (C5 and C6) differ only in that drifts observed under alkaline conditions are negative. Otherwise, deposition potential seems to have very little effect on the drifts observed (except at very low pH values).

It would be difficult and somewhat pointless to measure precise values for the drifts encountered. It is sufficient to state that, as the solution becomes more alkaline, the electrode will tend to display an increasing tendency to drift. At pH 8,

this can be as much as 25 mV in 5 hours. Under acid conditions, the tendency for the potential to drift is much less pronounced, displaying, at pH 4, negative drifts of around 10 mV over the same time period, while under even more acid conditions (approximately pH 2), the maximum potential drift over a period of 20 hours varied from +6 mV in the case of electrode C3 to +16 mV in the case of electrode C6. The above values refer to measurements made in U.B.4 solution, exposed to the atmosphere, crossing the pH scale from high to low pH values.

A further observation which should be mentioned, at this stage, was the tendency, in some cases, for potentials to rise or fall to maximum and minimum values and then proceed to drift in the opposite direction. This suggests the presence of at least two opposing processes.

The initial transients observed when electrodes of this type are introduced into solutions and the subsequent potential drifts vary with the solution concerned. Figures 6.24, 6.25 and 6.26 show the transients observed from three typical solutions, a phosphate mixture, a carbonate-bicarbonate buffer and sodium hydroxide (0.1 M). It can be clearly seen that the phosphate solution yields the smallest initial transient (Figure 6.24), while the sodium hydroxide gives the greatest transient (Figure 6.25). Hydrochloric acid (0.1 M) yields an initial transient similar to that of the carbonate/bicarbonate buffer solution (Figure 6.26). In these figures, the dots or crosses show the e.m.f. obtained from electrode C3 while the blank sections indicate the periods over which it was impossible to monitor potential for experimental reasons. The e.m.f. of a glass-calomel cell in the same solutions

Initial Transient in Phosphate Buffer Solutions

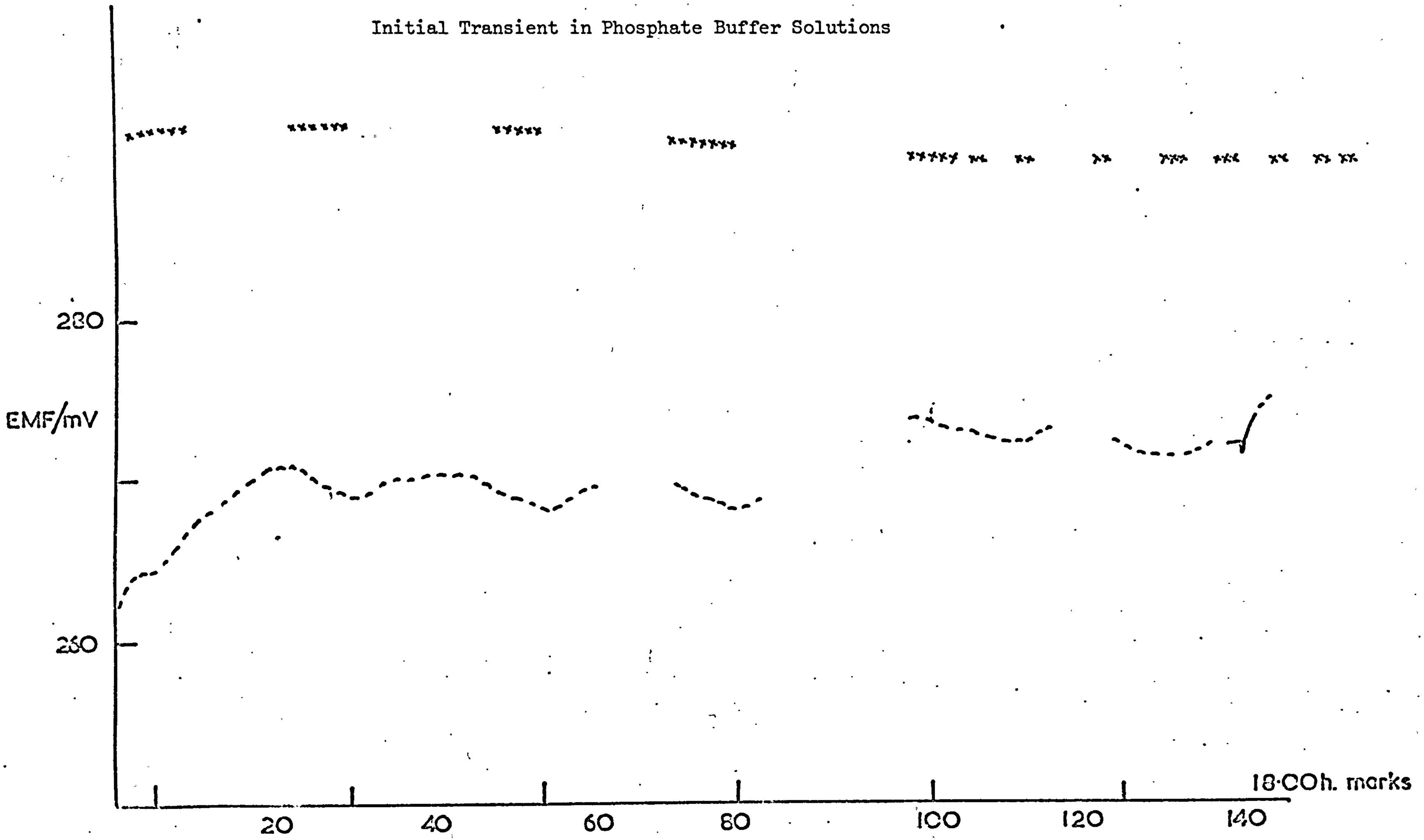
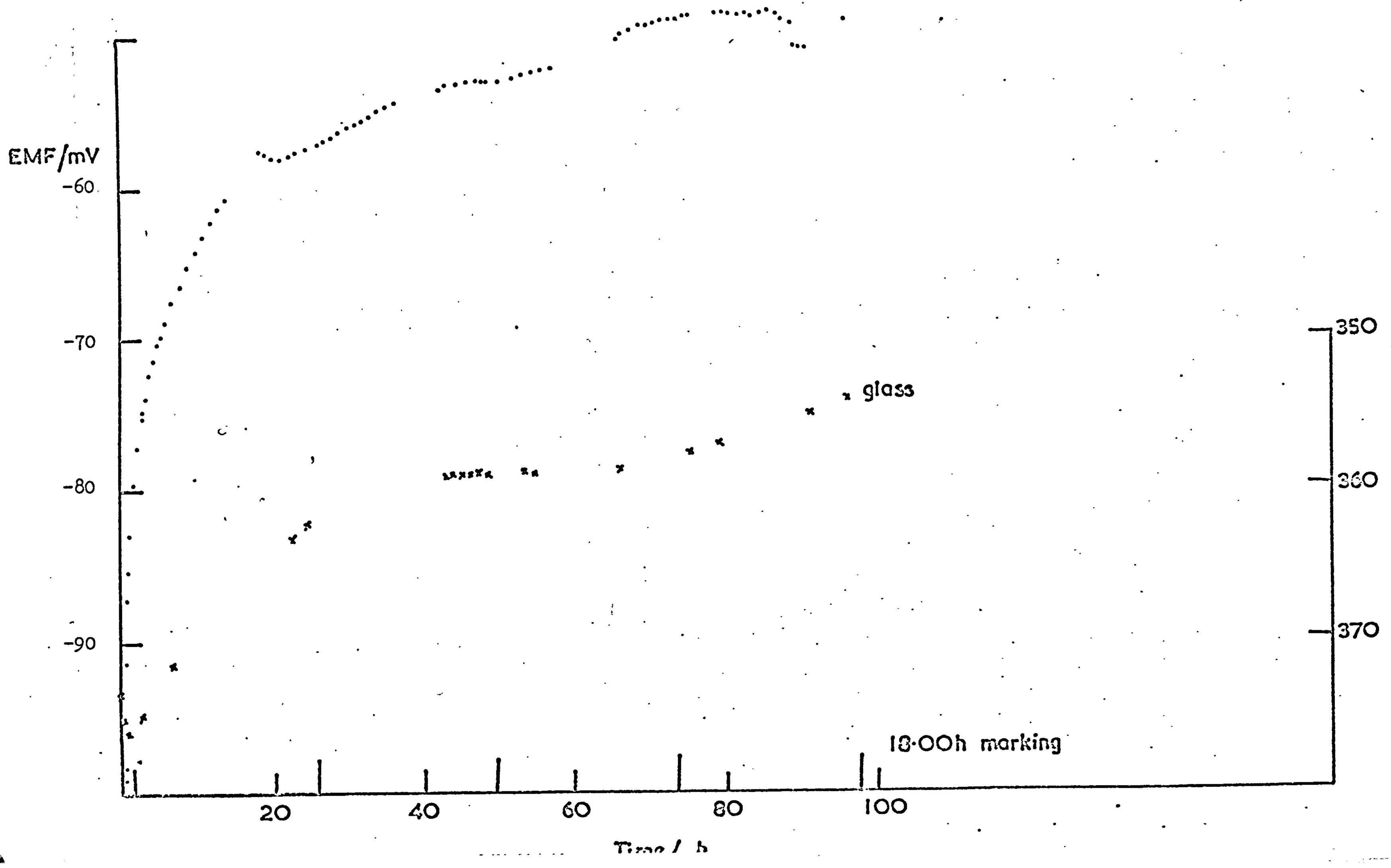


Fig. 6·24

Fig. 6·25 Initial Transient in Sodium Hydroxide Solution



Initial Transient in Carbonate Buffer Solution

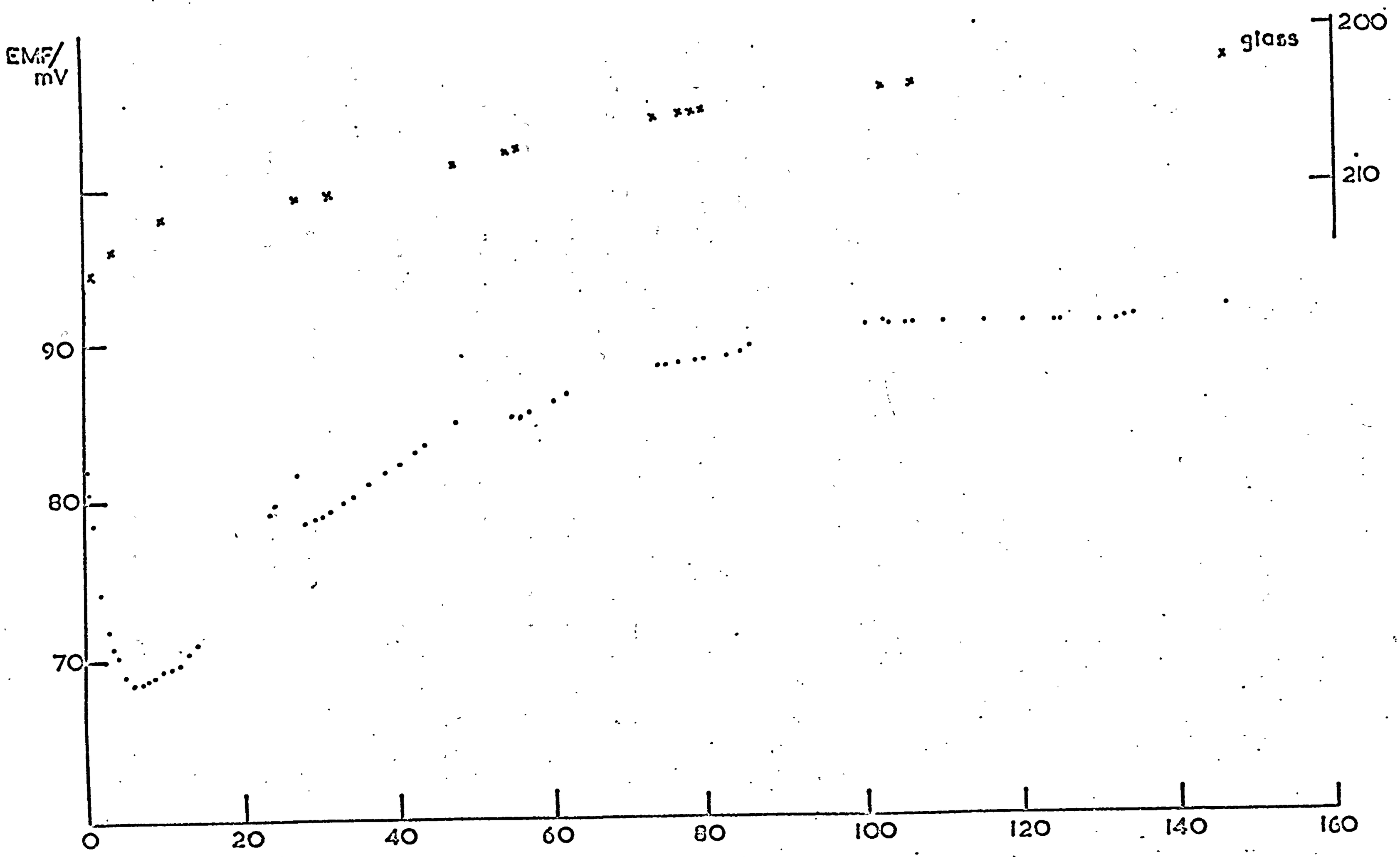


Fig 6.26

is indicated by a series of crosses.

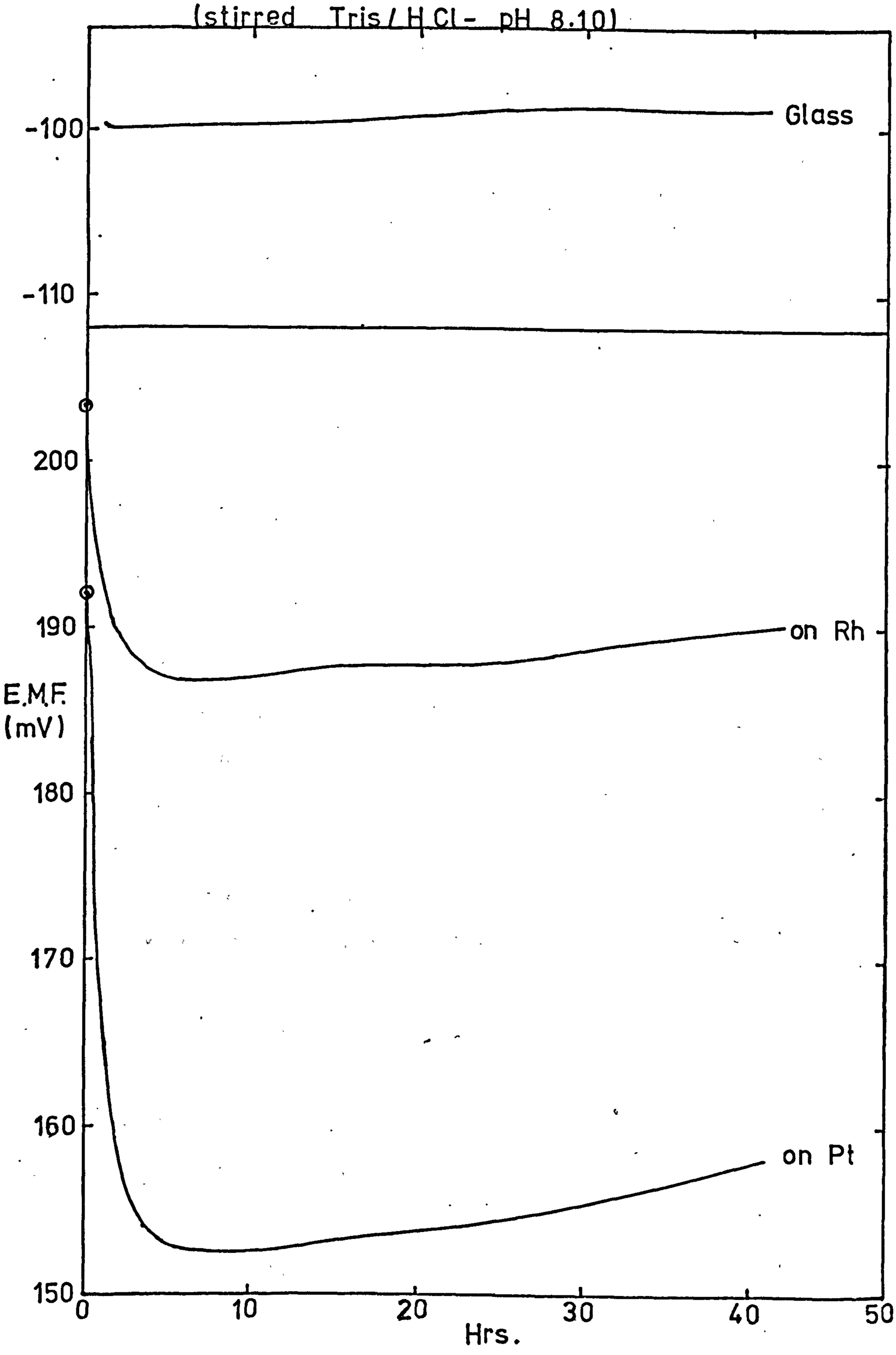
Figure 6.27 shows the initial transients obtained from a Tris/HCl solution using electrodes E1 and E3. It can be clearly seen that the transients are substantially reduced by the use of rhodium rather than platinum blanks.

One odd feature of this electrode system came to light while measurements were being made using the phosphate solution to determine initial transients: When an electrode was left in such a solution for a period of 140 hours and its electrode potential monitored, a pronounced slow oscillation became apparent. The amplitude of this oscillation was small (1 to 1.5 mV) but unmistakable. It was surprisingly regular on weekdays, the minima occurring from 6 pm. to 6.30 pm. and the maxima occurring from 8 to 10 am. On weekends, however, the pattern was interrupted by a 4 mV positive displacement of potential. An oscillation was still apparent but it did not possess the same regularity. Although this effect was most obvious in the case of the phosphate solution, partly due to the rapid equilibration of the electrode in this solution, an oscillation was also apparent in other solutions, particularly phthalate.

Although the deviation due to this oscillation is obviously small, it does clearly show that the electrode is susceptible to changes in the experimental conditions. It is difficult to decide which particular condition is responsible for this effect. The most likely cause is temperature variation. Other possible causes are the effect of light and changes in atmospheric oxygen. These effects are dealt with in sections 6.3 and 6.4. Changes in pH due to the absorption of carbon dioxide were ruled out

FIG. 6-27

EQUILIBRATION OF PLATED Rh ELECTRODES



since the glass electrode showed no such oscillation.

One important factor to consider when assessing any electrode is reproducibility. This word can be interpreted in two ways, firstly from the point of view of obtaining similar values from individual electrodes, and secondly in terms of obtaining reproducible values from similar solutions.

From the former point of view, it has already been shown that electrodes prepared using different plating potentials display a wide variation at high pH values. It has been found that potentials obtained from electrodes prepared by plating for 1.5 hours and 2.5 hours show a similar tendency to 'cross' just below neutrality thus reinforcing the conclusions drawn in section 6.1.4. A superficial assessment made on the basis of observations obtained from a few electrodes indicates that electrodes plated at the same potential yield e.m.f. values within approximately 0 to 5 mV. Clearly, for any certain conclusion to be made in this respect a large number of electrodes would have to be exposed to the same solution. This, however, was not within the capabilities of the apparatus employed. Subjective judgements made in the course of general experimental work seem to reinforce the observations made above.

If these values are true, reproducibility between individual electrodes is much poorer than in the case of glass electrodes but does show a very great improvement over the electrodes examined in Chapter 5 and compares favourably with the individual reproducibility of antimony electrodes.

Since the potentials obtained using this electrode system are prone to drift, it is obvious that great difficulties arise in

obtaining reproducible results, the potentials measured depending upon the time allowed for equilibrium. For this reason, the values obtained from stirred U.B.4 at pH 7 could vary from +195 to +237 mV. The experiment using individual solution referred to in section 6.1.4, yielded corresponding values within +230 to +235 mV.

In order to obtain some indication of the reproducibility of the system, an electrode was subjected to transfer between individual solutions and the potential values taken after 30 minutes. The potentials obtained from phosphate solution, after subjecting electrode G2 to aqueous sodium hydroxide (0.1 M) and to a solution of potassium hydrogen phthalate, were found to fall within a range of about 2 mV. The potentials obtained from phthalate solutions were found to be within a range of 5 mV.

This experiment shows that a certain degree of reproducibility is possible with this electrode system, although the results reported in this section in general clearly show that it is quite unsuitable for reference purposes or precision use as indicator electrode.

6.3 Effects of Experimental Conditions

6.3.1 The Effect of Temperature on Electrode Potential

In section 6.2 references were made to a daily oscillation of electrode potential and possible causes were given. Temperature variation was eliminated as the cause because no outright correlation could be found between the electrode potential and temperature

readings on a Hewlett Packard Quartz thermometer (Type 2801A), although a substantial temperature fall was observed on weekends. It is important, however, that the temperature coefficient of any electrode system should be known.

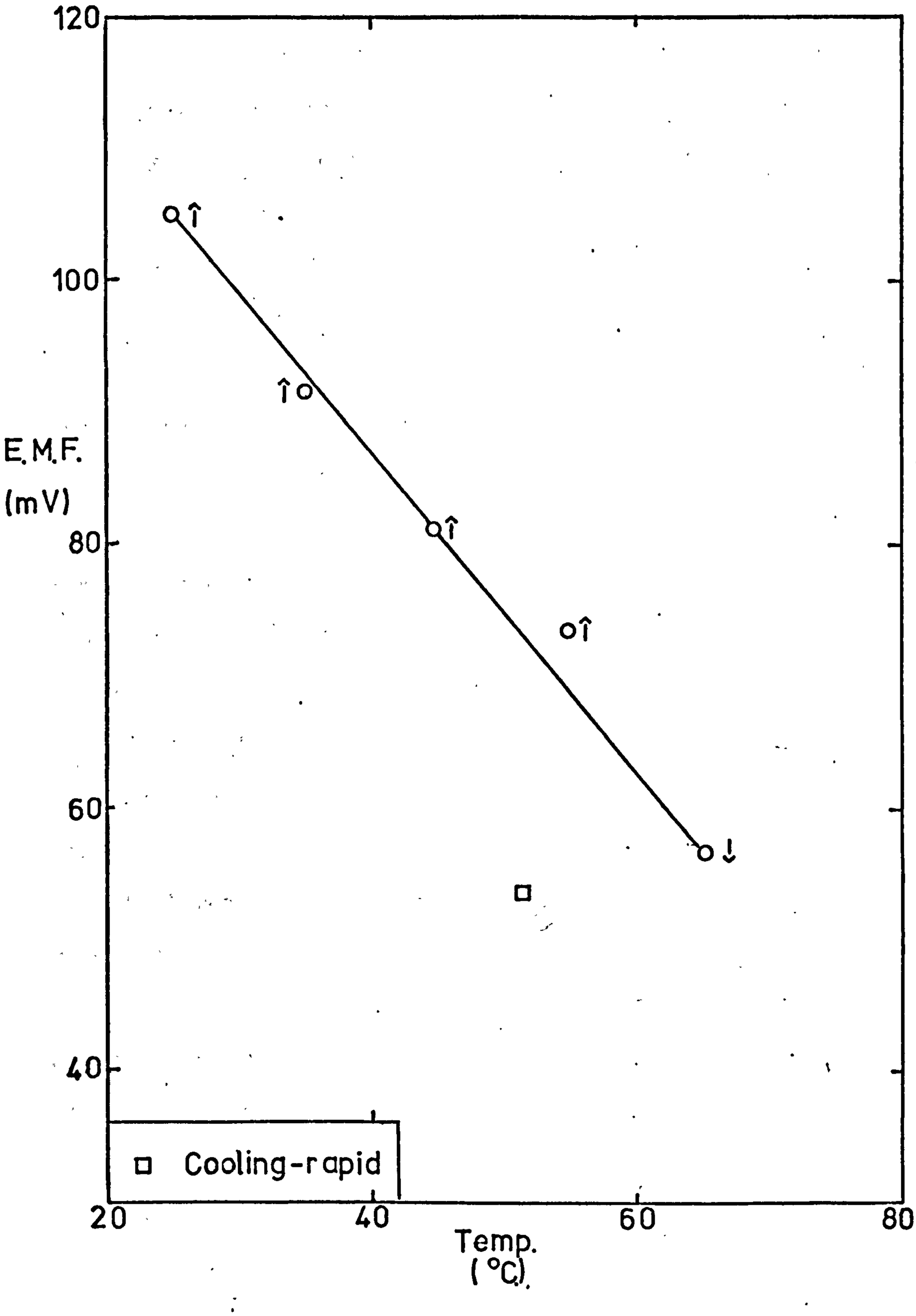
In this work, this measurement was achieved by means of an insulated waterbath in conjunction with a Tecam 'Tempunit'. Temperatures were measured by means of a Quartz thermometer and electrode potentials were measured in the usual way.

Figure 6.28 shows how the e.m.f. of the electrode D1-calomel cell varies with temperature. The overall potential variation is about -1.2 mV per degree centigrade. The temperature coefficient of the glass-calomel cell was found to be -0.05 mV per degree over the same range. If the temperature dependency of the calomel electrode potential is in the order of -0.7 mV per degree,[12] the temperature coefficients of electrode D1 and the glass electrode become -1.9 mV and 0.75 mV per degree centigrade. From these results, it is clear that, although electrode D1 has a temperature coefficient far in excess of that of the glass electrode, it compared favourably with the antimony electrode which has a temperature coefficient of 2 to 3 mV per degree centigrade.[2]

A single point on Figure 6.28 gives an indication of the amount of hysteresis obtained. Other experiments show that the extent to which hysteresis is observed decreases as the temperature falls. The arrows shown on Figure 6.28 indicate the direction of potential drift. It can be seen that up to a temperature of about 60°C, this is in the positive direction. At this point a reversal takes place and the potential begin to drift rapidly in

FIG 6·28

TEMPERATURE VARIATION



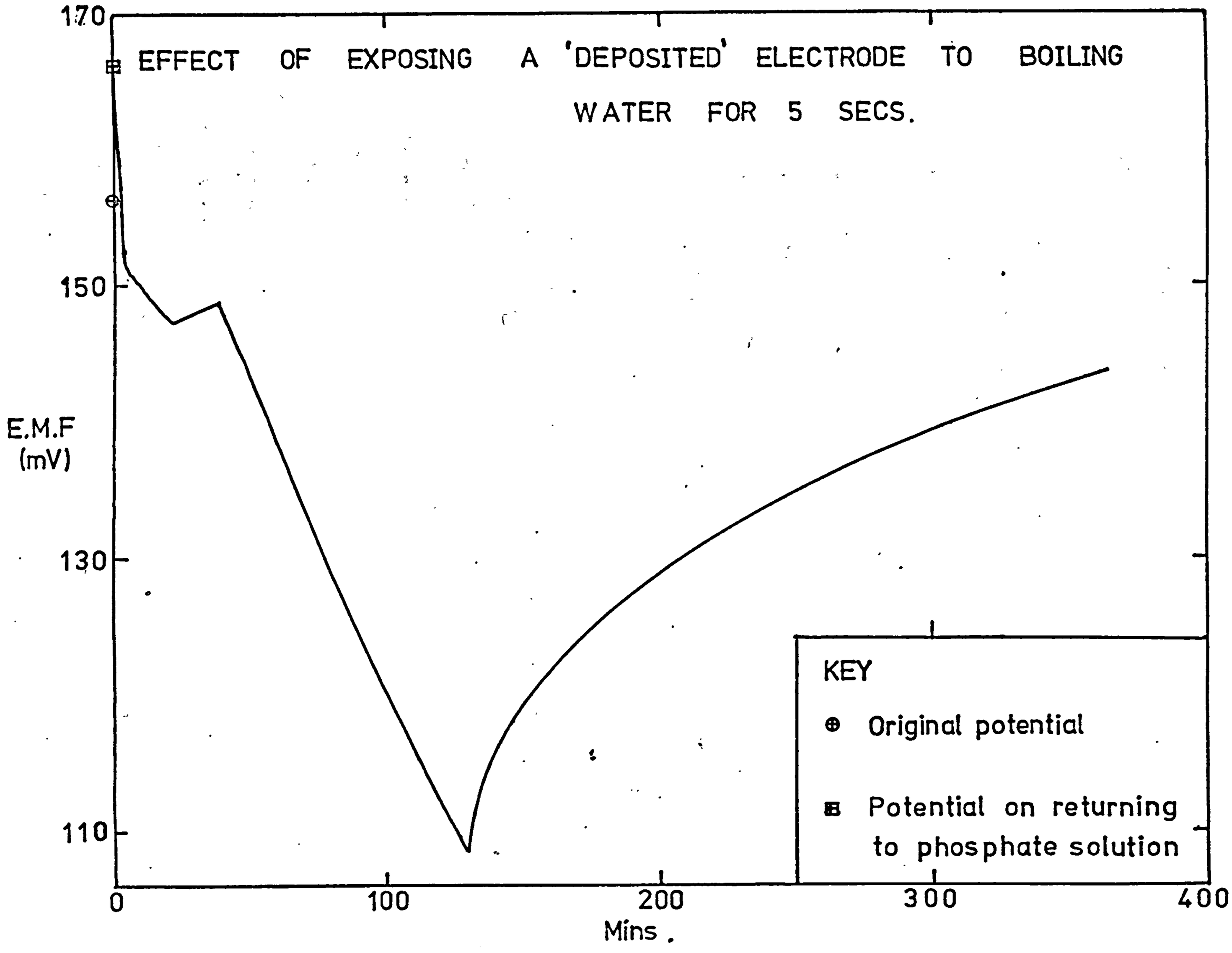
the negative direction.

It is difficult to assign a definite reason for this departure, but some possibilities may be postulated. Firstly a chemical change in the electrode material may take place, secondly a change in the physical nature of the material may be involved, a change in the chemical composition may take place and lastly expansion of the platinum 'base' within the glass 'stem' and may result in stress effects manifesting themselves.

In addition to carrying out straightforward temperature dependence experiments, the effect of temperature shocks was also examined. This was carried out by first allowing electrode D1 to equilibrate in phosphate solution (pH 6.99) ate 25°C. After removing the electrode from solution, it was exposed to boiling distilled water, returned to the phosphate solution and the recovery of the electrode potential recorded.

It was discovered that when the electrode was exposed to boiling water for 1 second, the only effect observed was a positive displacement of e.m.f. by about 20 mV. However, the electrode potential recovered its original value within 2 minutes. On more prolonged exposure to boiling water (5 seconds), it was found that, although the e.m.f. was first displaced by a similar amount, a similar recovery was not observed. Instead, the e.m.f. 'passed' its original value and reached a much more negative potential before finally regaining its original value. Figure 6.29 shows how the e.m.f. varied during one such experiment. The electrode behaviour under these conditions was not reproducible but a catastrophic negative displacement was also observed in other cases. It is likely that this behaviour is caused by stress

FIG. 6-29


EFFECT OF EXPOSING A 'DEPOSITED' ELECTRODE TO BOILING WATER FOR 5 SECS.
170
150
130
110
E.M.F (mV)
0
100
200
300
400
Mins.
KEY
Original potential
Potential on returning to phosphate solution

effects due to differential expansion and contraction of glass and metal. This negative displacement could account for the negative drift observed when the solution temperature was raised above 60°C.

6.3.2 The Effect of Light on Electrode Behaviour

It is unlikely that variations in lighting could be responsible for the oscillation referred to previously, because the maxima and minima observed do not correspond to extremes of lighting, and secondly because it would be impossible to explain the anomalous weekend behaviour.

It is known, however, that light does have an effect on some metal electrodes although this effect seldom exceeds a few millivolts.[74] Except where the metal is covered by a photo-sensitive film (e.g. AgBr), exposure to light normally gives a more positive potential.[74]

The following general photo-effects were listed by Young,[49,75]

1) The reduction of oxygen and hydrogen overpotential on metals such as platinum which do not have insulating films on the surface.

2) Electronic photoconduction in insulating oxide films, including a change in potential under constant current and open circuit conditions or a change in current at a constant potential.

3) Changes in potential of electrodes with non-insulating oxide films, e.g. the potential of platinum which has been heavily oxidized by A.C. and D.C. has been reported to become more

positive under certain conditions on exposure to ultra-violet light. These changes could be due to an alteration in composition due to irradiation and also by the production of transient species in solution.

4) Potential changes due to variation in corrosion rates have also been reported.

Experimental observations on the effect of light on electrode potentials are complicated by its direct heating effect.[74] Also, attempts at excluding light can interfere with the functioning of devices for temperature control. Measurements obtained from experiments which involved covering the apparatus were discarded for this reason, even though some potential changes were observed.

In the present work, the assessment of the influence of light on electrode potentials has been restricted to simple qualitative judgements. It was found that light from laboratory fluorescent fittings had no effect on the electrode potential, but when an Ultra Violet source was directed at the electrodes through the walls of the glass vessel a positive potential drift resulted. The greater part of the U.V. spectrum should be absorbed by the glass walls. Therefore, the potential drift must be due to some other portion of the spectrum emitted by the source. Temperature variation would cause a negative drift of potential. On the other hand, when the source was directed at the polypropylene electrode holder, a negative drift of potential took place. The resulting displacement of potential was permanent in nature, although the electrode potential did drift back towards its original value, to a certain extent. This effect could be

attributed to changes in the nature of the solution, since on changing the solution the original value was approached.

6.3.3 The Effect of Stirring

As was seen in the previous chapters, the presence or absence of stirring often has a crucial effect on the electrode potential of metal-metal oxide electrodes. Any assessment of stirring effects on these electrodes is complicated by the effect of stirring on the liquid junction of the reference electrode used. For this reason, before examining this effect, it was first necessary to examine the response to stirring of the glass-calomel cell. The experiments quoted below were carried out in Tris/Cl solution (pH 8.10).

When stirring was curtailed, it was discovered that the e.m.f. developed by the glass-calomel cell was displaced to the negative side by 2 mV $\pm$ 0.25 mV and this new value was maintained for 30 hours. When stirring was recommenced, the e.m.f. regained its original value. When electrode E3 was subjected to the same treatment, an identical initial displacement was observed, but over a period of approximately 5 hours, the e.m.f. drifted back to within $\pm$ 0.1 mV its original value, and this value was maintained for another 25 hours. When stirring was resumed, the process was reversed. If results obtained from the experiments conducted with the glass-calomel are used to compensate for variations due to the reference electrode, it can be seen that electrode E3 is, in fact, responsible only for the long term variations mentioned previously.

After the solution had been purged with nitrogen and the electrode allowed to equilibrate in unstirred solutions, the stirrer was switched on and the changes in e.m.f. recorded. As expected, the e.m.f. showed an instantaneous positive deflection of 2 mV. Apart from this, the net response was a further drift of potential to a steady value 1.5 mV more positive than the 'displaced value'. When stirring was discontinued, the e.m.f. immediately fell by -1.75 mV, and after 5 minutes began to drift in the negative direction.

It is, therefore, clear that the electrode potential responds quite differently to stirring in aerated and deoxygenated solutions. This offers further proof that the electrode potentials must be controlled by different reactions under aerated and deoxygenated conditions. It would be impossible, however, to give reasons for this since the nature of the electrode surface is not exactly known.

6.4 The Effect of Oxygen Concentration in Solution on Electrode Potential

In section 6.2, reference was made to an 'intriguing' daily oscillation of potential. One possible cause suggested in that section, was a daily variation of the concentration of oxygen in solution. The fact that the ventilation system in the laboratory is switched on daily at 8 to 9 am. and switched off at 5 pm., and remains off at weekends added credence to this suggestion.

This section relates to attempts at controlling the oxygen partial pressure in the atmosphere above the solution and hence the oxygen concentration in solution and then examining the

subsequent effects on electrode potential. Before this can be done, it is essential that the factors concerning the equilibrium between the concentration of oxygen in solution and its partial pressure in the surrounding atmosphere, should be fully understood. Subsection 6.4.1 deals with these aspects.

6.4.1 The Solubility of Oxygen and Nitrogen in Aqueous Solutions

If the phase rule is applied to a system of a gas and a liquid solvent, since there are two components and two phases present, it is easily seen that the system has two degrees of freedom, i.e. the phase rule

$$F = C - P + 2 \qquad 6.12$$

becomes

$$F = 2 - 2 + 2 = 2 \qquad 6.13$$

This means that both temperature and pressure have to be fixed in order for the equilibrium to be completely defined.[76]

Two coefficients are used to express the extent to which gases dissolve in liquids. The first, which was proposed by Bunsen in 1857, is known as the absorption coefficient (α). This is defined as the volume of gas, reduced to S.T.P., dissolved by unit volume of solvent at the temperature of the experiment under a partial pressure of 1 atmosphere, i.e.

$$\alpha = v_o / Vp \qquad 6.14$$

where v_o is the volume of gas dissolved (reduced to S.T.P.)

V is the volume of the solvent and p is the partial pressure of the gas in atmospheres.[76]

Another coefficient, put forward by Ostwald (1888) is known as the coefficient of solubility (β). This is defined as the volume of gas, measured under the temperature and pressure at which the gas dissolved, taken up by unit volume of liquid, i.e.

$$\beta = v / V \qquad 6.15$$

where v is the actual volume of dissolved gas. Using the gas laws, this can be related to v_o by the expression:

$$v = Tv_o / T_o p \qquad 6.16$$

where T is the experimental temperature and T_o is 273 K.

Combining these equations, an expression equating α to β may be obtained:[76]

$$\beta = \alpha T / 273 \qquad 6.17$$

It has been previously demonstrated that the solubility of gases in a liquid solvent varies with both temperature and pressure. Generally, as the solution temperature increases, there is a decrease in the amount of gas dissolved. The effect of varying the partial pressure of a gas in contact with a solution, however, is crucial to the method used for controlling the concentration of oxygen in solution and therefore will be dealt with in greater detail.

Very simply, an increase in pressure has the reverse effect on solubility to that of temperature, i.e. an increase in pressure increases the mass of oxygen dissolved. This relationship may be expressed quantitatively by Henry's Law (1803) which states that, the mass of gas dissolved by a given volume of solvent, at constant temperature, is proportional to the pressure of the gas with which it is in equilibrium,[76] i.e.

$$m = k'p \qquad 6.18$$

where m is the mass of gas dissolved in unit volume of solvent.

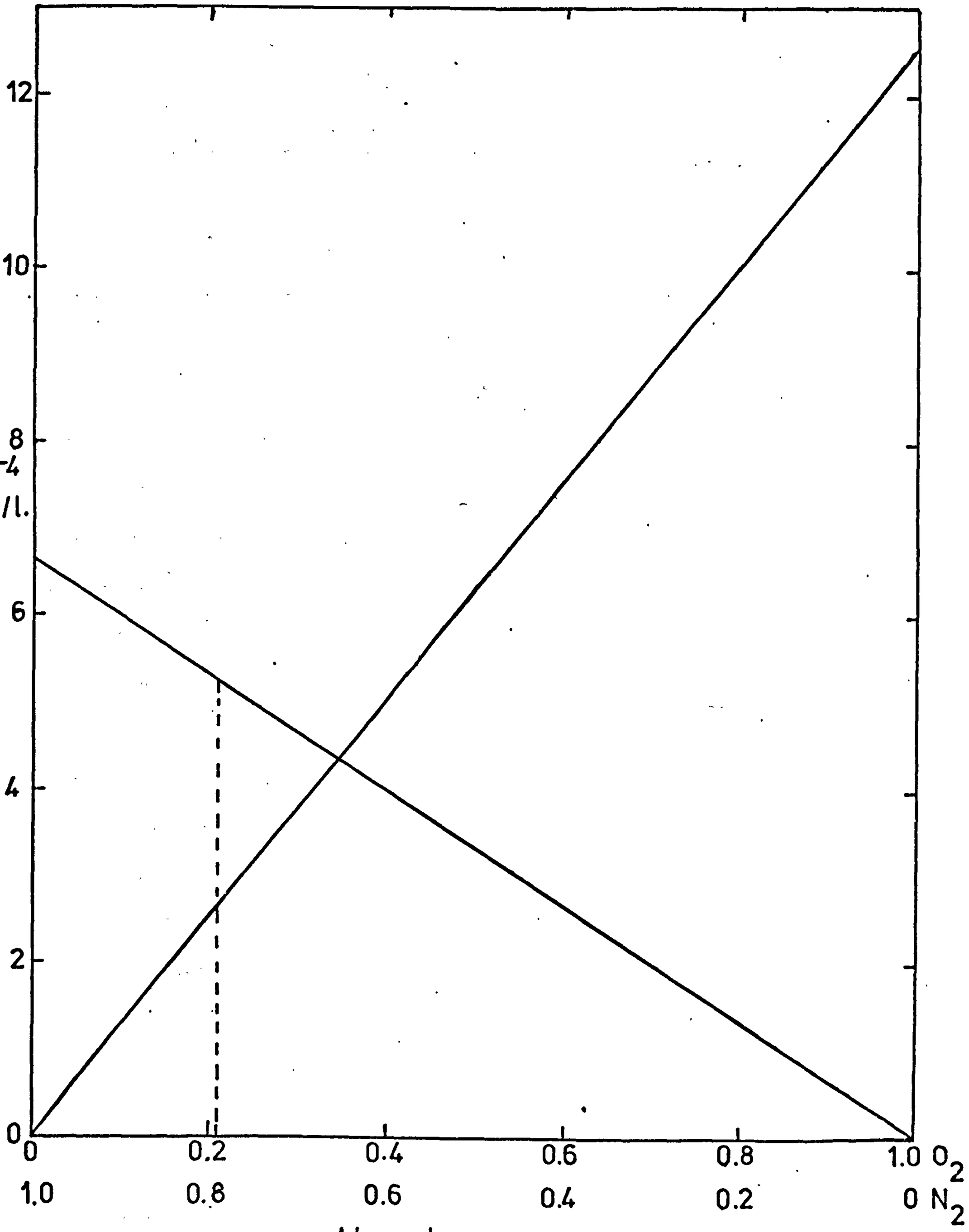
It can be shown, using Henry's Law and Boyle's Law that, the volume of gas dissolved, measured at the experimental pressure, is independent of that pressure.[76]

If the solvent is in equilibrium with a gas mixture rather than a single gas, the number of components in the system will be increased from 2 to 3, therefore, from the Phase Rule it can be easily calculated that the system will have 3 degrees of freedom. Therefore, it is now necessary to fix the composition of the gas as well as the temperature and pressure in order for the composition of the liquid phase to be defined.

It was shown by Dalton (1805) that each constituent of a mixture of gases dissolves to an extent dependent only on its own partial pressure. This means that Henry's Law applies to each gas independently of the pressure of the other gases.[76] Therefore, the solubility of each gas can be calculated on the basis of its own partial pressure, as shown in figure 6.30, and therefore, as far as the solubility of oxygen is concerned, the mixture of gases

FIG.6·30

SOLUBILITY OF OXYGEN AND NITROGEN IN WATER (25°C)



present in air can be replaced by a mixture of oxygen and nitrogen in such proportions that the partial pressure of oxygen in the mixture remains the same. In figure 6.30, the partial pressure of oxygen in air is represented by a dotted line.

As far as this investigation is concerned, this relationship is important, in that it permits the mass of oxygen in solution to be controlled by means of varying the partial pressure of oxygen in the surrounding atmosphere.

The oxygen concentrations quoted in this section of the work have been calculated on the basis of Bunsen absorption coefficients for distilled water, quoted by Orcutt and Seevers.[77] The values quoted for oxygen and nitrogen are, respectively, 0.0281 and 0.0149. These values are reported to be reliable in a review by Markham and Kobe[78] which also cites a number of references containing information for other gases dissolved in various solutions. Bunsen absorption coefficients are particularly useful for this work since it is a simple matter to convert these values to concentrations in terms of moles per litre. This can be done simply by dividing α by 22.4 litre.

One complication in calculating the solubility of gas mixtures lies in the fact that gases tend to be less soluble in aqueous solutions of electrolytes than in pure water. The extent of this "salting-out" effect is independent of the nature of the gas but does depend on the nature of the solute concerned.[76]

Since both phosphate and universal buffer solutions were employed in this section of the work, it was decided that it would be virtually impossible to determine the effects on gas solubility of the numerous electrolytes employed in the buffers.

Consequently, oxygen concentrations have been calculated on the assumption that the gas is dissolved in distilled water. Obviously, this is an oversimplification, and as a result, concentrations quoted in figure 6.31 should be regarded merely as the extent to which the concentration of oxygen in solution changes during the experiment and not as absolute concentrations. It is more correct to quote oxygen partial pressures and these have also been supplied on this figure.

6.4.2 Experimental Methods

The apparatus used to control oxygen partial pressure is similar to that employed by Short.[4] A full description of the apparatus is given in Chapter 2 and permitted a nominal variation of oxygen partial pressure from 2×10^{-2} to 1 atmosphere.

Short,[4] who was investigating the effect of variations of oxygen partial pressure on antimony electrodes, declares that in general, electrochemical equilibrium was slow to be obtained. This was also found to be the case for the electrodes used in this investigation. For this reason, measurements were mainly confined to those oxygen partial pressures in the vicinity of atmospheric partial pressure.

Before commencing experiments, the solutions concerned were first purged with nitrogen for several days. The solutions were stirred throughout the experiments and readings were taken with increasing oxygen content. This procedure was recommended by Short,[4] since it was observed that, in that case, the electrodes equilibrated more rapidly in the direction of increasing oxygen

pressure. In the present work, gas mixtures were bubbled for 30 to 60 minutes and then the electrodes were allowed to equilibrate. After a suitable period of time, the process was repeated. This cycle was repeated until the experimenter was satisfied that the e.m.f. obtained was constant. This method was adopted since it reduced gas wastage and prevented errors caused by continued bubbling.

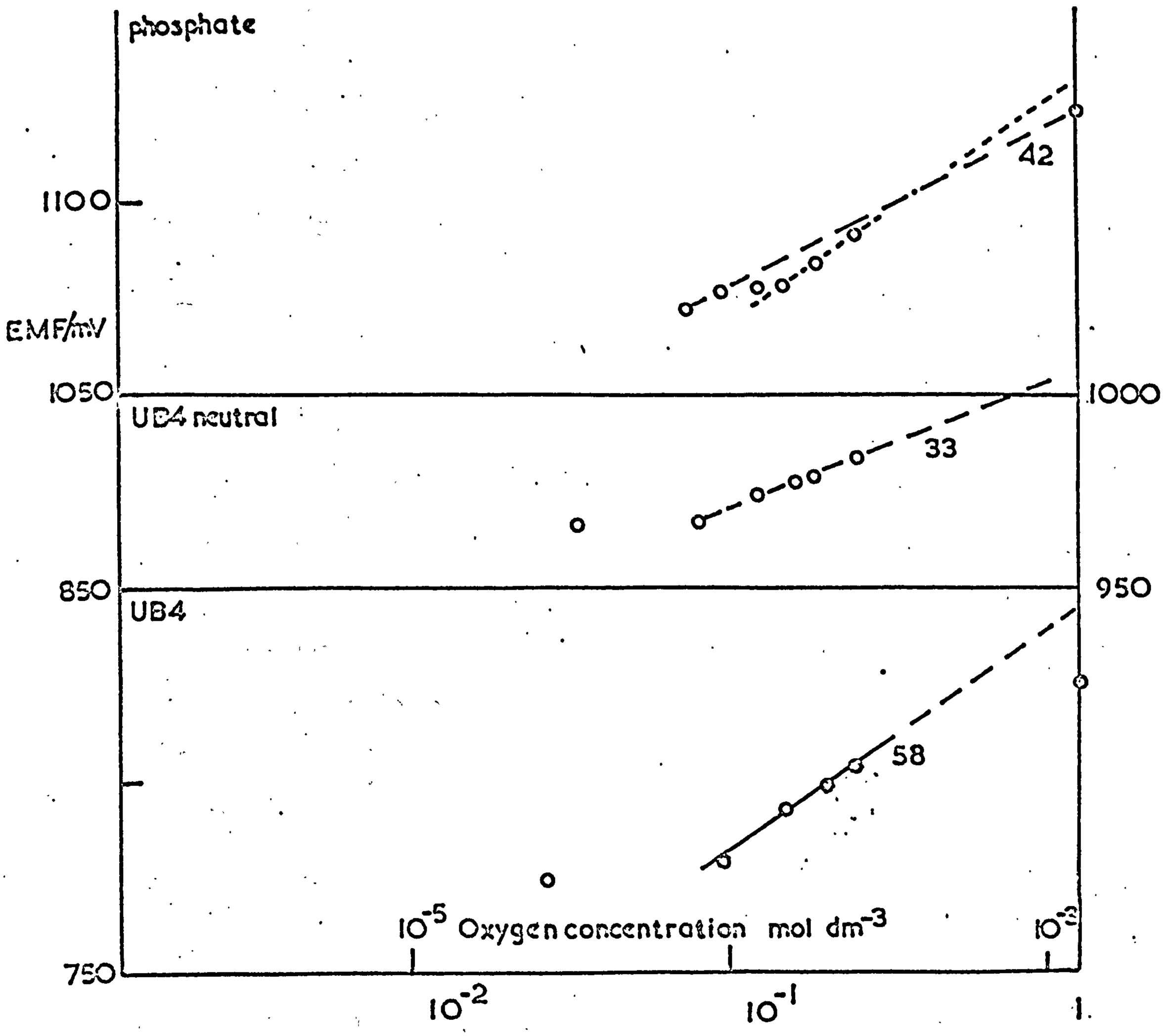
Three solutions were used in this section of the work, phosphate (pH 6.99), U.B.4 (neutralized with 0.25 M hydrochloric acid) and U.B.4 (pH 10.4). Changes in pH were compensated for by means of e.m.f. values obtained from the glass-calomel cell.

6.4.3 Results

E-$\log_{10}P_{O_2}$ plots for each solution are given in figure 6.31. Electrodes G1, G2, G3 and G4 were all subjected to this treatment but readings from electrode G2 have been quoted as being representative of the system. It can be seen that, for both universal buffer solutions, the plots have a linear portion. The plot obtained from the phosphate solution, on the other hand, shows a marked change of slope, but for the higher oxygen partial pressures, a slope of 57.5 mV. log $P_{O_2}{}^{-1}$. A decrease in slope appears generally to take place at both extremes of oxygen partial pressure, but this could be accounted for by errors inherent in the oxygen mixing apparatus. Changes of slope, such as these, were reported for some solutions by Short,[4] but for the purposes of this work, these are irrelevant since only changes of oxygen partial pressure in the region of atmospheric oxygen partial

Fig.6·31

Effect of Variations of Oxygen Partial Pressure



pressure are of interest.

6.4.4 Inferences

It will be recalled from Chapter 5 that Rh-O alloys would be expected to yield potentials which are invariant with respect to oxygen partial pressure. It will also be recalled that rhodium electrodes with adsorbed oxygen films would be expected to have potentials which vary with oxygen partial pressure to the extent of 15 mV per log P_{O_2}, since the O_2/H_2O reaction would probably predominate.

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O \qquad 6.19$$

The results obtained in this investigation show that, on the linear portion of the plot, the e.m.f. varies with log P_{O_2} by gradients close to '60 mV log $P_{O_2}{}^{-1}$ and 30 mV log $P_{O_2}{}^{-1}$. Neither of these mechanisms could account for these gradients.

It is very difficult to determine the reactions responsible for these gradients but two possible explanations are given below. A log P_{O_2} response of 60 mV could be explained by the following reaction:

$$O_2 + H^+ + 1e \rightarrow HO_2 \quad (60 \text{ mV log } P_{O_2})^{-1} \qquad 6.20$$

while a response of 30 mV log $P_{O_2}{}^{-1}$ could be explained by a similar reaction:

$$O_2 + 2H^+ + 2e \rightarrow H_2O_2 \quad (30 \text{ mV log } P_{O_2})^{-1} \qquad 6.21$$

These reactions were discussed with reference to platinum by Hoare.[50]

If these reactions are correct, it remains to be explained why they should differ according to the pH of solution. One connection with pH is obvious if the stoichiometry of the reactions is examined. It is even more difficult to account for the change of slope in phosphate solution. A somewhat similar change of slope was reported by Short[4] for the antimony electrode, however. A change of reaction obviously must take place, but it is not clear what property might induce such a change.

When a solution is purged with nitrogen, the observed e.m.f. changes by as much as -200 mV. The variations reported above could not possible account for a variation as great as this. It is, therefore, clear that purging with nitrogen must also have a direct effect on the electrode surface, perhaps changing the degree to which oxygen is absorbed on the electrode surface.

The fact that the electrode potential is susceptible to changes in oxygen partial pressure in the surrounding atmosphere could account for the daily oscillation of observed e.m.f. described in section 6.2.

6.5 Examination of the Surface of Rhodium Deposited Electrodes

It will be recalled that in section 1.5 of this chapter, the assertion was made that, in the appraisal of an electrode for reference or pH purposes, not only should its zero current behaviour be examined but also kinetic aspects associated with

the system. A knowledge of the physical and chemical properties could be extremely useful in the interpretation of results obtained in the pursuance of these aims.

In this investigation the physical structure of the electrode surface was studied by means of a Stereoscan microscope while EDAX and X.P.S. (E.S.C.A.) were used in the elucidation of the chemical nature of the system. A brief description of these techniques and the results obtained with them are given in the ensuing sections.

6.5.1 Stereoscan Photographs

Electronmicroscopy is well known as a technique for the examination of microscopic structures in biology and other physical sciences. This is an instrument similar in purpose to the ordinary light microscope, but with a much greater resolving power. Whereas, in the operation of the latter a beam of light is used to illuminate the object, instead a beam of electrons from an electron gun is used. As the beam of electrons passes through the object, differential scattering occurs resulting in an image being carried on in the beam. This image, after being magnified by a magnetic or electrostatic focusing apparatus is displayed on a fluorescent screen and recorded photographically.

The main disadvantage with the above system is that the object studied has to be very thin indeed in order that the electron beam may pass through. Clearly, for the purposes of this investigation, since the samples in question are of a quite substantial nature, this disadvantage would render the technique

useless. Fortunately, an instrument which permits the examination of the surface of three-dimensional items is now available. This instrument is known as the scanning electron microscope or simply Stereoscan.

The operational principle involved in this technique is very similar to that described for the electron microscope in the preceding paragraphs, the main difference being that an image is obtained from 'secondary' electrons emitted as a result of bombardment of the surface material by the electron beam rather than the transmitted counterparts. As its name implies the instrument continually scans the sample permitting its entire surface to be examined. Since the varying contours of the sample surface will result in a differing amount of scattering, an image can be built up on the screen as before.

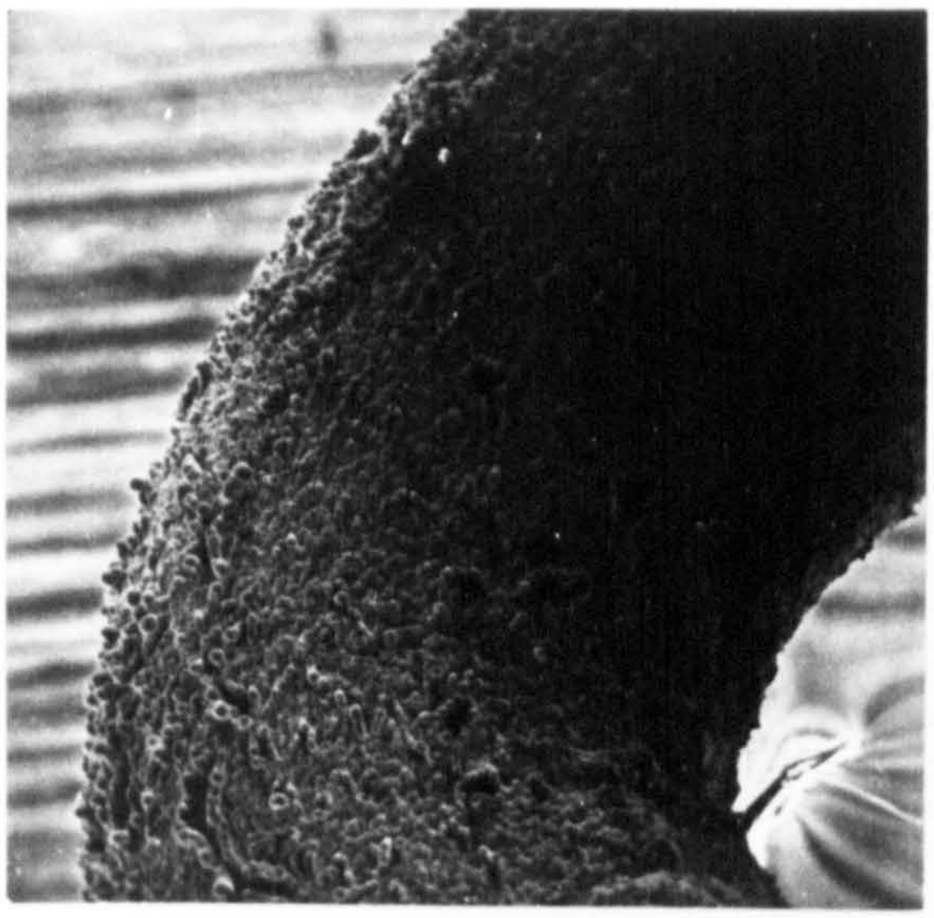
The first sample to be examined using this technique was electrode B1 (see Table 6.1). The electron micrographs of the surface of this sample are shown on plate 6.1. Even at the comparatively low magnifications illustrated on plate 6.1.1 an intricate structure is obvious. Plate 6.1.2 shows the same sample subjected to a higher magnification. A number of dark 'pits' are clearly visible but it is impossible to tell whether these are inclusions of oxide (or some other compound) or merely depressions in the rhodium surface, perhaps even penetrating down to the platinum 'base'. Plate 6.1.3 not only clearly shows these 'pits', but also outward growths.

The second sample (B2) to be examined in this way was also investigated using X.P.S. (see section 6.5.3). It can be clearly seen from plate 6.2.1 that the surface has a much smoother

PLATE 6.1

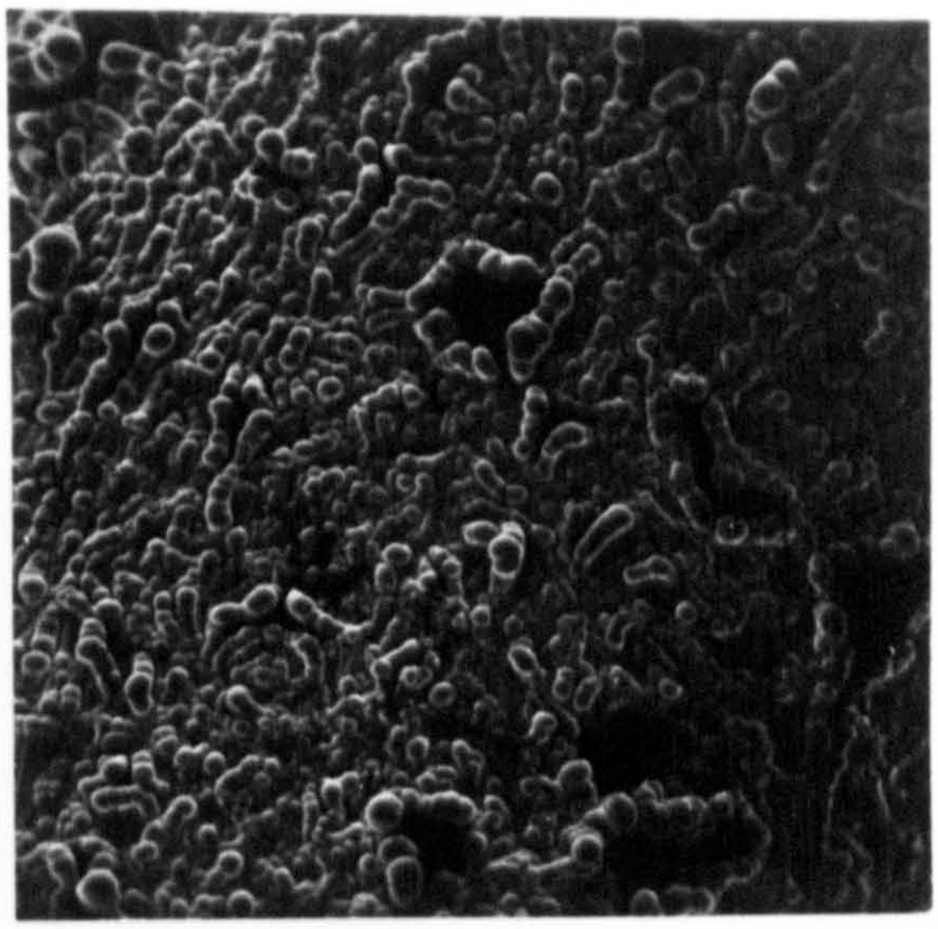
RHODIUM PLATED ON PLATINUM WIRE

6.1.1



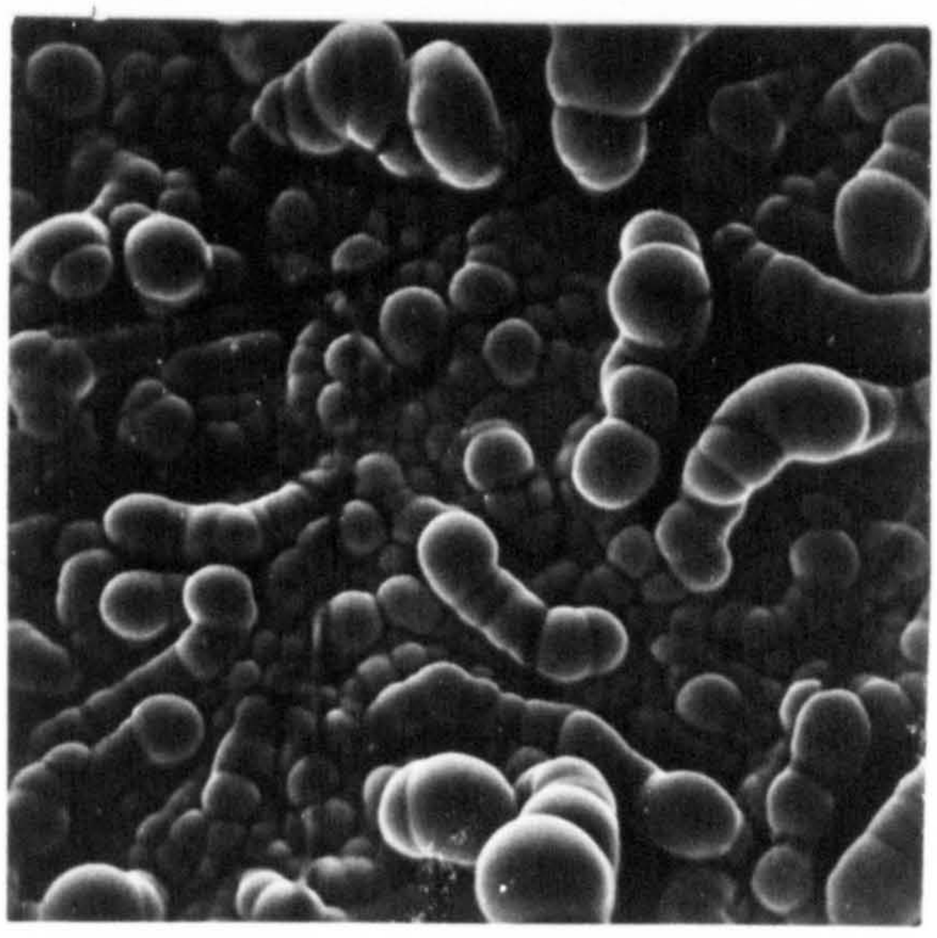
x 190

6.1.2



x 475

6.1.3

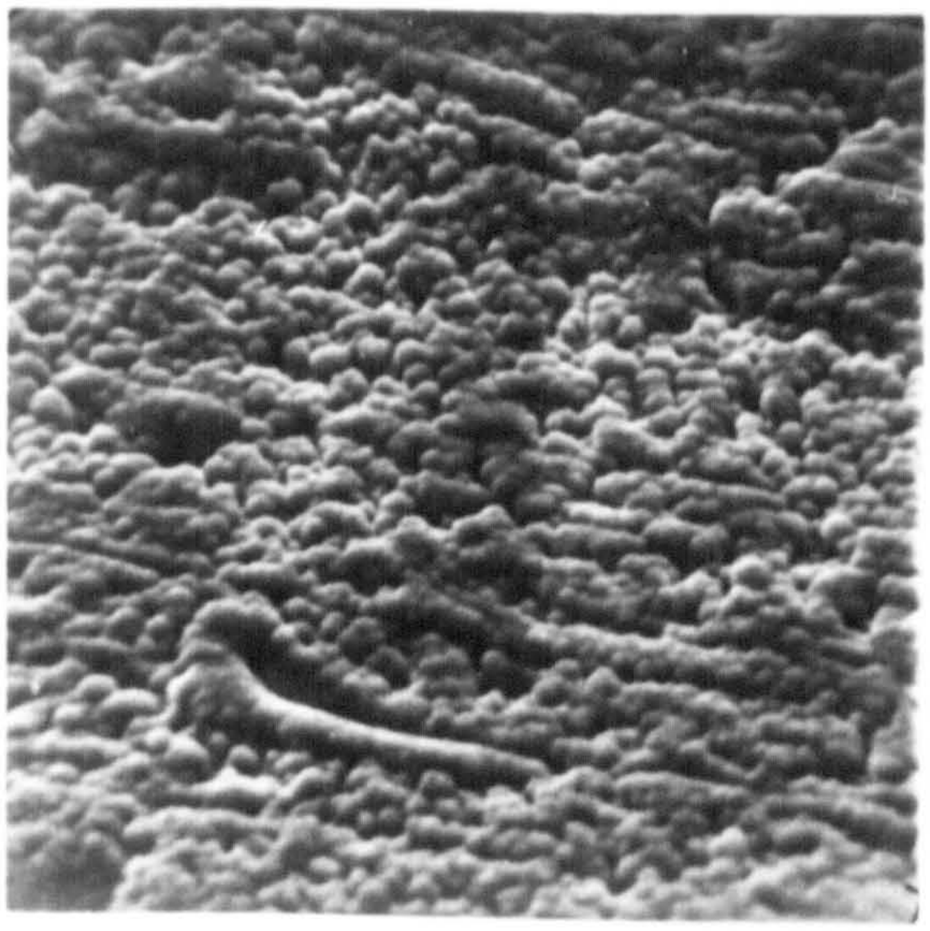


x 1900

PLATE 6.2

RHODIUM PLATED ON PLATINUM FOIL

6.2.1

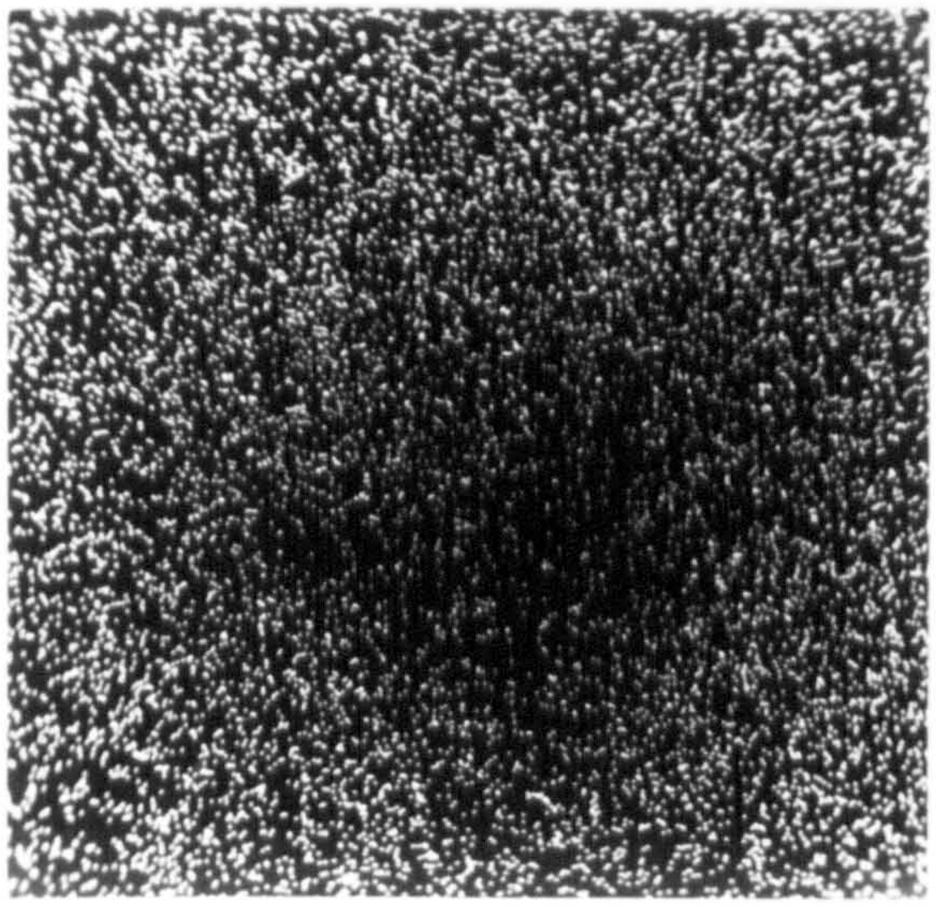


x 5,000

6.2.2

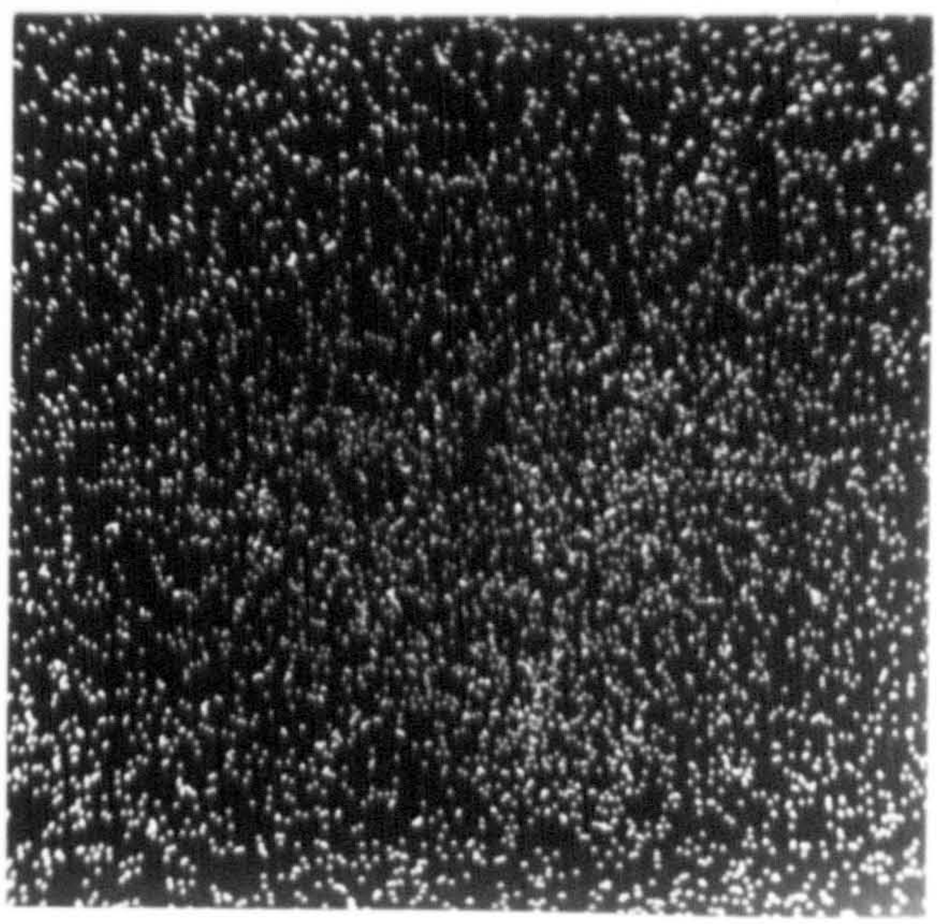
x 50,000

6.2.3



RHODIUM X-RAY DISTRIBUTION
x 50,000

6.2.4



PLATINUM X-RAY DISTRIBUTION
x 50,000

appearance, even at 2.5 times the maximum magnification used on the previous sample. The 'pits' observed on sample B1 are absent except for one or two smaller examples.

The significance of these results will be discussed in the summary in section 6.5.4 along with those from sections 6.5.2 and 6.5.3.

6.5.2 EDAX Studies

When the metal sample is subjected to bombardment by an electron beam, x-rays with energy characteristic to the element concerned will be emitted as a result of atomic excitation. The technique which makes use of this phenomenon to identify and determine the quantity of elements present in a particular sample is known as Energy Dispersive Analysis or EDAX. Since an electron beam is incorporated in the scanning electron microscope an EDAX facility can be included in the instrument, thus enabling stereoscan photographs to be compared with analyses obtained in this way.

The photograph illustrated in plate 6.2.2 shows one of the small 'pits' in plate 6.2.1 magnified 10 times. At such magnifications the resolution of the instrument deteriorates, consequently a blurred image results. In this case, however, it is included solely for the purpose of relating the x-ray distributions shown in plates 6.2.3 and 6.2.4 to the actual structure of the specimen. The white dots shown on plate 6.2.3 indicate the density of x-rays characteristic to rhodium, emitted, while on plate 6.2.4 the density of x-rays emitted from platinum is

recorded.

It can be clearly seen from plate 6.2.3 that far less rhodium can be detected in the centre of the 'pit' than on its rim. The reverse is true (to a lesser extent) for platinum on plate 6.2.4. These observations prove that the 'pits' are true depressions and not merely inclusions of oxide. If the latter were true, almost as much rhodium would be detected in the 'pit' as around its rim. The fact that rhodium can be detected in the centre of the pit shows that, for this particular electrode, the platinum 'base' is not directly exposed to the exterior. It is likely, in view of the coarser structure that the pits shown in plates 6.1 penetrate to the platinum surface.

6.5.3 X.P.S. Studies

Having established that electrodes prepared in the manner described do in fact possess a substantial film of rhodium-containing material, it now remains necessary to establish the nature of this layer. The most straightforward methods available involve the chemical removal of the film and its subsequent testing by physical and chemical means. Unfortunately for noble metals, procedures such as these are fraught with difficulties owing mainly to the pronounced similarities in physical and chemical properties of platinum and rhodium and their respective compounds.

Firstly, it is almost impossible to ensure that only the deposited film is removed. Secondly, even if this is achieved, spurious results can be obtained when comparing different compounds

containing the same noble metal. This problem is well illustrated in the case of platinum by the work of Anson and Lingane and the subsequent comments of Breiter and Weininger.[50] Also, tests for rhodium are very similar to those for other noble metals.[70] Furthermore, there is no guarantee that the materials present on the electrode surface will not be altered chemically in an unforseen manner by the stripping process employed. Indirect chemical methods would obviously be useless if the "overweight" is due to the presence of some form of dermisorbed oxygen (as suggested in section 6.1.1) since any occluded oxygen would be released as soon as the metal lattice is broken up.

In view of the problems associated with indirect chemical methods, it was decided to rely upon spectroscopic techniques. In this investigation electron spectroscopy was used because of its convenience of application and its ready availability.

X-ray photoelectron spectroscopy is a technique for determining the binding energies of electrons in molecules by measuring the energies of electrons ejected due to the bombardment of a molecule by a monoenergetic beam of x-rays or photons.[79] In this investigation the technique which has also been referred to as E.S.C.A. (Electron Spectroscopy for Chemical Analysis) has been employed.

In this technique, the sample under investigation is held in an evacuated chamber where it is bombarded with essentially monochromatic x-rays. The electrons that are emitted as a result of this are analyzed according to their kinetic energy (K.E.). The incident energy of the x-rays ($h\nu$) is known and fixed; therefore, the binding energy (B.E.) of the ejected electrons may

be determined from equation 6.22.

$$h\nu = \text{K.E.} + \text{B.E.} \qquad 6.22$$

Since an x-ray source is used of 1253.6 eV energy, electrons may be ejected from core orbitals. As all elements except hydrogen and helium have such orbitals, they may all be detected using this technique. Thus initially the elements present in the sample may be determined.

However, the binding energy of a particular core orbital for a particular element shifts according to the charge on the ion in its particular environment. This "chemical shift" of binding energy may enable the oxidation states of the elements present to be determined.

Since the number of electrons of a particular energy emitted is proportional to the number of ions in that environment, the technique is semi-qualitative.

In this investigation the application of X.P.S. has been restricted to the qualitative determination of the various elements present in a particular sample as well as changes in their chemical environment on the basis of the binding energies of their electrons. For reasons which will become apparent, quantitative aspects have been largely ignored, with the exception of some rather imprecise assessments.

Apparatus

All X.P.S. measurements in this investigation were carried out

using an AEI ES200B electron spectrometer, the x-rays being produced by means of electron bombardment of a magnesium target. The pressure in the sample chamber was typically 10^{-7} to 10^{-8} torr.

Procedure

For the purposes of this investigation, X.P.S. has been used to try and determine the chemical composition of the surface layers of the rhodium plated electrodes. These preliminary results are not analyzed in great detail but the spectra are compared with spectra of known entities and of previously established binding energies.

The samples prepared for investigation by X.P.S. were plated on platinum foil 'spades' (0.5 cm x 1.5 cm). Cleaning was effected by means of hot aqua regia and distilled water as described in section 6.1.2 and electrical contact with the electroplating apparatus (see sections 6.1.2 and 6.1.3) was achieved by a small hooked platinum 'side-arm' on the sample and a corresponding platinum hook embedded in glass.

The samples were polarized cathodically at 400 mV for the periods given in table 6.2 and then washed briefly in two volumes of triple distilled water. The five samples were then subjected to the pretreatments described below.

Two samples were prepared as above and then transferred to triple distilled water for storage. A third sample was washed briefly and then subjected to heating in an open furnace at $325^{\circ}C \pm 10^{\circ}$, for 30 minutes. At the end of this time the sample was removed and quickly transferred to a stoppered sample tube

Table 6.2

Sample	Steady Polarization Current (to nearest 10μA)	Plating Time (mins.)	Treatment
B2	Unknown	150	None - except was used for EDAX prior to ESCA
F1	40	90	None
F2	30	90	'Baked' in air
F3	40 to 50	90	Soaked in phosphate solution
F4	50	90	Soaked in U.B.4 solution

previously flushed with nitrogen. The fourth sample was placed in a phosphate buffer mixture at pH 6.99 for several days while the fifth was exposed to U.B.4 solution. The latter two samples were subjected to these pretreatments in order to determine to what extent the electrode surfaces are affected by exposure to these materials. Phosphate buffer was chosen for this purpose because the potentials of these electrodes appear to show less tendency to 'drift' in this solution than in others. U.B.4, on the other hand, was selected because the presence of amines in solution could be responsible for the tendency of potentials to 'drift' away from the theoretical potential - pH line (see section 6.1.4).

A problem concerning the washing of these electrodes becomes apparent at this stage. If the samples are not washed sufficiently, the materials present in solution could be carried over physically into the spectrometer, while if the electrode is permitted to soak in water for long periods of time, any adsorbed materials could be removed by leaching. It is clear that a compromise is required and this was achieved by washing each sample in 6 separate volumes of triple distilled water over a period of twenty minutes.

The samples prepared were placed in the instrument in the evacuated chamber and exposed to the x-ray beam. The energies of the emitted electrons were then recorded and the intensity of the signal produced was plotted against the energy of the electrons emitted (see Table 6.3).

Table 6.3

Binding Energy Region Studied (eV)	Element Investigated[+]	Orbital[*] Excited
77 - 67	Platinum	4f
317 - 307	Rhodium	3d
199 - 189	Chlorine	2p
537 - 527	Oxygen	1s
407 - 397	Nitrogen	1s
171 - 161	Sulphur	2p
69 - 59	Sodium	2s
147 - 137	Phosphorus	2p
287 - 277	Carbon	1s

[*] These orbitals were chosen either because they are the most intense for the element concerned or because they have been previously studied.[58]

[+] Since a sample heated in an open furnace is prone to contamination and likely to acquire impurities, the investigation of sample F2 has been restricted to the examination of rhodium, platinum and oxygen.

Results and Inferences

Electron peaks due to the presence of rhodium were detected from all the samples. The spectra showed pronounced asymmetric peaks which are likely to correspond to the presence of oxide and metal. The baked specimen (F2) showed an even more pronounced shoulder. This is due to the presence of a thicker layer of oxide/hydroxide. The pretreatment would probably be expected to increase the amount of oxide present (Figure 6.32).

Platinum was detected in all cases barring sample B2. One possible reason for this observation may be the gradual dissolution of platinum at the anode during the plating process but this is unlikely (see section 6.1.3). It is more likely that platinum escaped detection in sample B2 because of the thicker rhodium layer deposited on the platinum surface. The escape depth of the electrons excited by the x-ray bombardment depends on their kinetic energy and is in the range 30-40 Å. The mass of the rhodium layers deposited on the samples can be calculated by means of Faraday's Laws (taking the current passing as 50 μA) to be in the order of 5×10^{-4}g for sample B2, and 3×10^{-4}g for the other samples. By taking the density of rhodium as 12.4 g cm^3 and the geometrical area as 1.25 cm^3, the thickness of the rhodium films can be calculated approximately to be 3,000 Å on sample B2 and 2,000 Å on the other samples.

At first sight, it would, therefore, appear that this thickness would exclude any possibility of penetration to the platinum surface by the x-ray beam. However, the above calculation does not take into account any roughness on the surface of the platinum blank

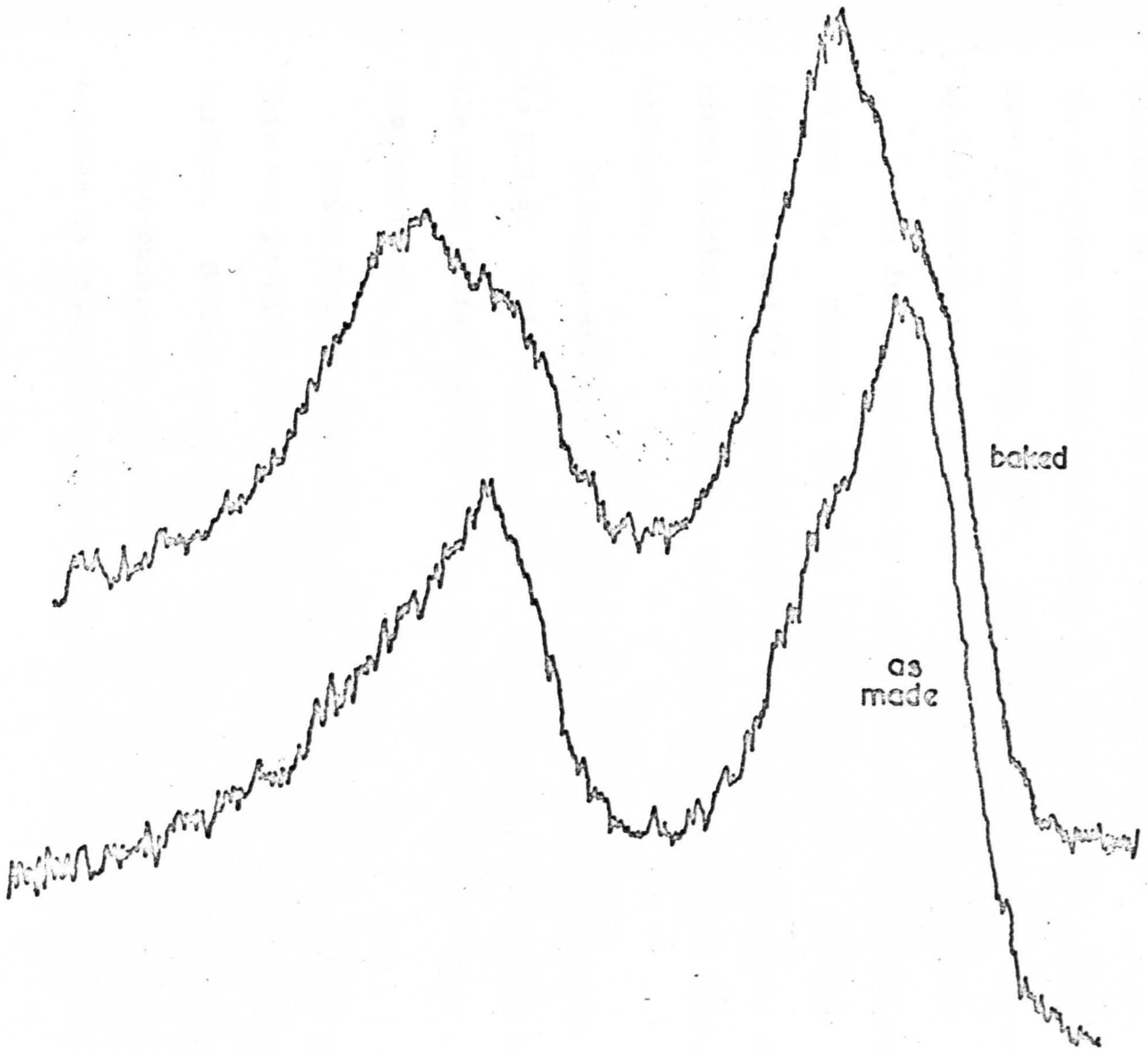


Fig. 6-32 Rhodium 3d XPS Spectra

and the presence of growths and pits such as those described in sections 6.5.1 and 6.5.2. The simple calculation quoted above also assumes that the plating process has a 100% current efficiency. Bearing in mind reports[62] that the current efficiency for this particular process is "remarkably low", this would be an unreasonable assumption, and so it is likely that the thickness of the metal film is considerably smaller than the value quoted above.

Oxygen spectra obtained from samples B2, F1, F3 and F4 indicate the presence of two bulk oxygen containing species. These could possibly be assigned to oxide oxygen and hydroxyl oxygen. For the spectrum obtained from sample F2, one of these 'peaks' is far more pronounced (fig. 6.39). This observation could be explained by the conversion of hydroxide or hydrated oxide to oxide.

Peaks due to chlorine 2p electrons were detected in samples F3 and F4. However, the fact that no signal was obtained from samples B2 and F1 suggests that this is due to incomplete washing since neither the phosphate buffer nor U.B.4 solution contain chlorides.

Nitrogen was not detectable in any sample except that exposed to U.B.4. This could be due to some form of interaction between the amine buffer substances and the rhodium surface (e.g. complexation).

Small traces of sulphur were detected only in sample B2. This was probably due to incomplete washing of the electrode surface. Sodium could not be detected in any of the samples.

The phosphorus spectrum was only examined for the sample exposed to phosphate solution. The presence of phosphorus

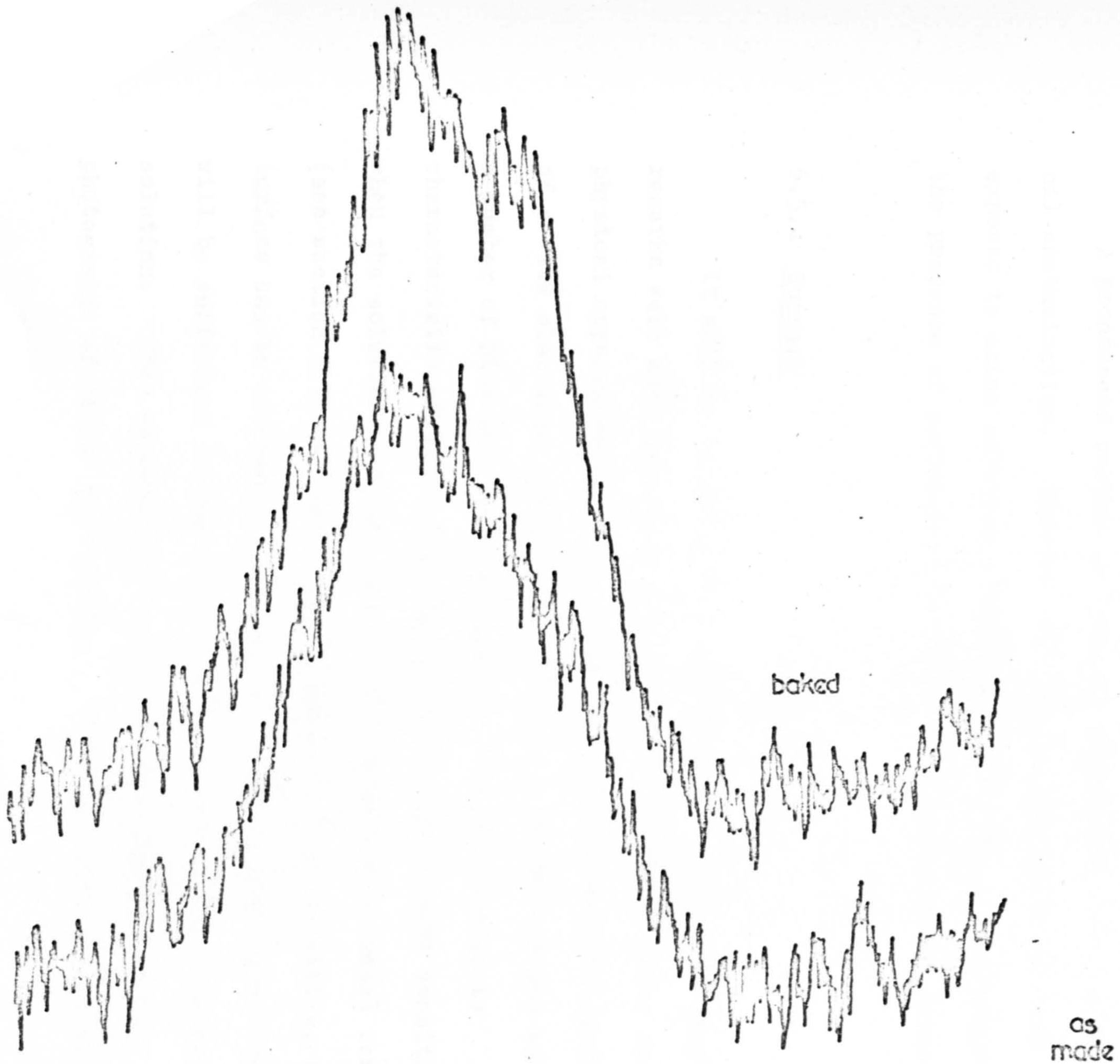


Fig.6·33 Oxygen 1s Spectra

containing species was unmistakable but was manifested in the form of two distinct peaks (fig. 6.34). For this particular element a single peak would be expected.[58] Thus the phosphorus is present on the electrode surface in two forms, possibly $HPO_4^=$ and $H_2PO_4^-$ since the buffer mixture consists of disodium hydrogen phosphate and potassium dihydrogen phosphate. However, when a sample of the phosphate buffer mixture was examined, a single peak was observed, therefore phosphorus must be influenced by some other factor.

A pronounced carbon 1s peak is always observed due to pump oil contamination. However, for the sample which had been exposed to amine solution a very asymmetric C_{1s} peak suggests the presence of carbon-containing species other than hydrocarbons.

6.5.4 Summary

It will be recalled that, in section 1.1 of this chapter remarks were made regarding the effect of current density on the physical appearance of metal deposits. Stereoscan photographs of a wire electrode indicated an intricate coarse surface with a number of pits and outward growths. This condition is characteristic of crystal growth at very high current densities, when the solution near the electrode is depleted of metal ions (see section 6.1.1). At slightly lower current densities, the surface can be expected to become fine grained since mass transport will be sufficient to deal with the removal of metal ions from solution. This expectation is borne out by the Stereoscan photographs of 'foil' electrodes. It would be desirable to

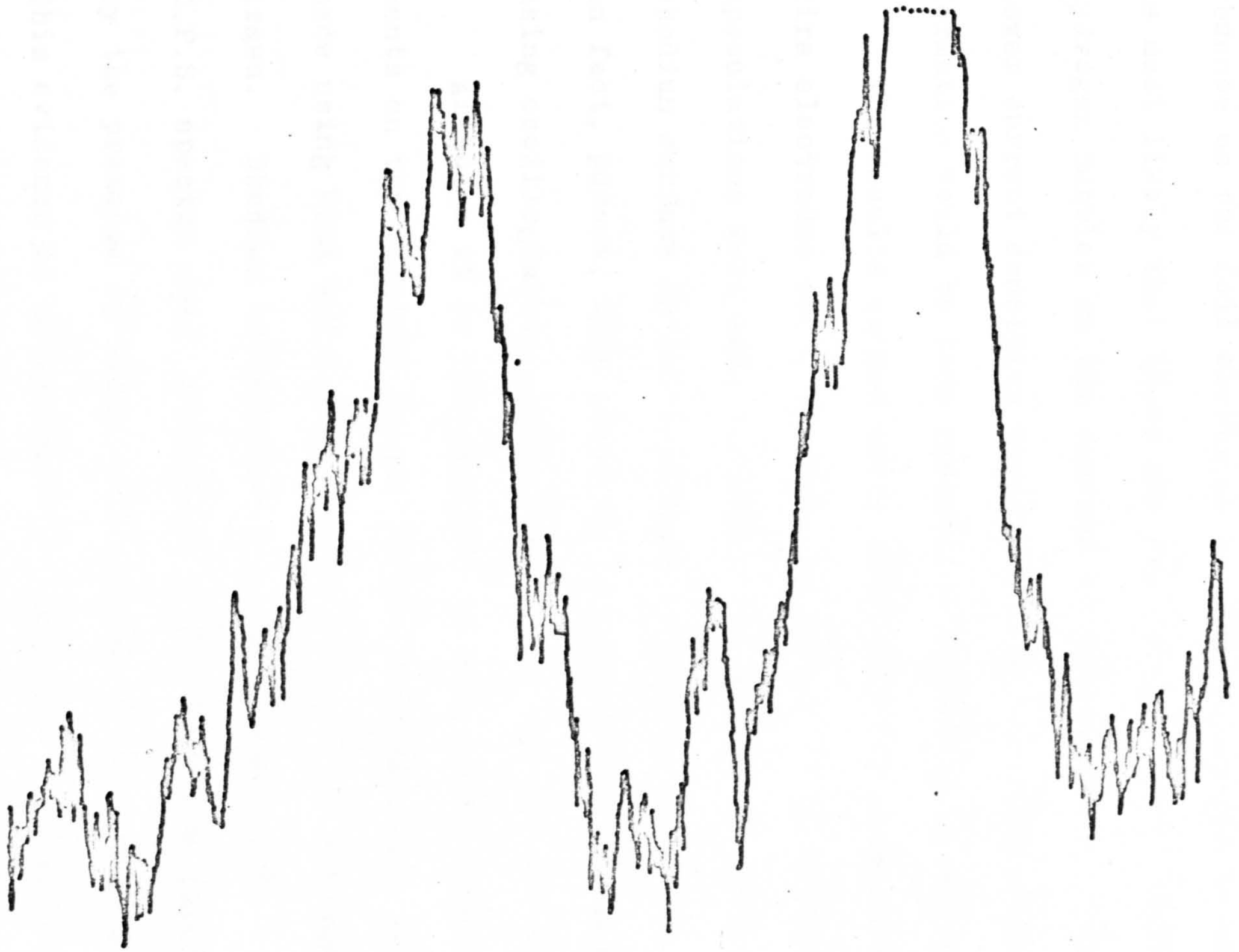


Fig. 6·34 Phosphorus 2p XPS Spectrum of Sample exposed to Phosphate Buffer.

illustrate this difference by the corresponding current density values, unfortunately instrument malfunction made this impossible. However, it is reasonable to assume a higher current density for the wire electrode in view of its much smaller surface area.

The growths observed on the wire electrodes are easily accounted for by crystallites growing out towards regions of higher rhodium ion concentration (see section 6.1.1). The numerous pits observed on the wire electrode and their comparative absence on the foil electrode is more difficult to explain. It is most likely that these are due to the slow formation of hydrogen bubbles on the surface of the wire electrode. At the lower current densities experienced by the foil electrode, hydrogen formation would be less pronounced resulting in fewer such pits.

The results quoted above show that the rhodium deposits on wire electrodes must, in fact, be porous. In section 6.1.4, speculations were made regarding the effect of porosity of the rhodium surface on the electrode potential. If the surface is, in fact, porous, this would be in agreement with measurements made using oscillographic polarography (see section 6.1.5).

Although it is not possible to make any definitive pronouncements on the chemical nature of the rhodium film, the measurements made using EDAX and X.P.S. enable a number of conclusions to be drawn. Rhodium is detectable by both techniques. Rhodium X.P.S. spectra show asymmetric peaks which are apparently caused by the presence of oxide or hydroxide on the rhodium surface. This evidence is corroborated by the fact that oxygen spectra indicate the presence of bulk oxygen containing species. A comparison of the oxygen spectra with those obtained previously[58]

from oxidized metal surfaces suggests that the peaks may be assigned to oxide and hydroxide species. 'Baked' samples give rhodium spectra with peaks showing greater asymmetry and one of the peaks in the oxygen spectrum increases in intensity.

Since other elements (e.g. chlorine) cannot be detected on either B2 or F1, the 'overweight' cannot be due to the presence of such species (see section 6.1.1).

The spectra obtained from samples F3 and F4 show clearly that electrodes of this kind are very susceptible to adsorption of materials dissolved in the solution in which they are placed. Although these results show clearly that the electrode surface is prone to take up phosphate, this does not give any indication as to how this occurs. The processes most likely to be involved, however, are complexation and adsorption. It is also possible that the phosphate molecules may become trapped in the porous crystalline deposit. It is difficult to explain why the presence of phosphate should enhance the stability of these electrodes. If the suggestion made in section 6.1.5, that the sigmoid pH curve may be caused by the conversion of rhodium to its oxide, applies, it is possible that complexation may result in the stabilization of the oxide film.

Complexation of rhodium with amine substances is known to occur[80]. It has been previously suggested that gradual complexation of the oxide or metal with the amines in U.B.4 may result in a gradual drift of potential. The fact that nitrogen was detectable in sample F4 as well as some carbon (other than that resulting from pump oil contamination), tends to support this view. If the process of complexation is much slower than

in the case of phosphate, essentially the same process may result in inferior electrode behaviour rather than the enhanced behaviour noticed when phosphate is present in solution.

6.6 Summary

In this chapter, rhodium electrodes prepared by deposition have been subjected to a number of different investigations using a variety of techniques. It would be useful at this point, therefore, to collate the information set out in the preceding sections.

It has been shown that, when the pH of an aerated solution was changed continuously a theoretical response of 59 mV/pH was observed. When a stepwise titration was carried out, however, a sigmoid response became apparent. In addition, it has been shown that, when a universal buffer solution was purged with nitrogen, a completely different response was observed, both for continuous and stepwise experiments. Under these conditions, a higher slope was obtained under acid conditions than under alkaline conditions.

It has been indicated, in Chapter 1 and in section 6.1.5 that, it is desirable that the potential of a reference or indicator electrode should be controlled by a single reaction. It is abundantly clear, however, that this is not the case, and a number of attempts at determining the interfering reactions have been made in this chapter.

In the first place, it has been shown in sections 6.1.5 and 6.5, that the electrode surface is porous and therefore,

it is not surprising that the electrode potential shows signs of being affected by the platinum 'base' metal. However, even when the platinum 'base' is replaced by rhodium, potential drifts are still apparent. Thus, it is clear that other interferences are present.

One such interference is the effect of oxygen. It has been shown in section 6.4 that, the electrode potential is affected by the partial pressure of oxygen in the surrounding atmosphere. In this section the following reactions were postulated to explain the results obtained:

$$O_2 + H^+ + 1e \longrightarrow HO_2 \qquad 6.20$$

$$O_2 + 2H^+ + 2e \longrightarrow H_2O_2 \qquad 6.21$$

The H^+/electron ratio in these reactions would also explain the theoretical pH response of -59 mV/pH, observed when the solution pH was changed continuously. If the e.m.f.s measured were the result of mixed potential as suggested in section 5.1, the other reaction would depend on the oxide phase present:

$$Rh(O)_x + 2_xH^+ + 2xe \longrightarrow Rh + H_2O \qquad 6.23$$

$$Rh\text{-}O + 2H^+ + 2e \longrightarrow Rh + H_2O \qquad 6.24$$

$$Rh_2O_3 + 6H^+ + 6e \longrightarrow 2\ Rh + 3\ H_2O \qquad 6.25$$

For the electrode potential to be dependent on pH and log P_{O_2} , reactions 6.20 or 6.21 would have to be potential determining. It was also stated in that section that variations in the response to oxygen in various solutions could be associated with changes in the electrode surface in these solutions. The results obtained from X.P.S. (E.S.C.A.) measurements reported in section 6.5, suggest that this could be so, since elements present in both solutions could be detected on the electrode surface after being exposed to the relevant solutions.

In section 6.1.5, it was shown that a 2-electron process takes place at the electrode surface. In view of the remarks made previously, regarding the possible processes taking place, it is clear that yet another process must be present. The likely reaction is one of oxide formation and it is possible that this could be responsible for the sigmoid response mentioned previously.

The change of slope under deoxygenated conditions is more difficult to explain. Reactions 6.20 and 6.21, obviously cannot take place under such conditions. In that case, one or more of reactions 6.23, 6.24 and 6.25 should take over, and therefore, a theoretical pH response should result. This is not so, and therefore, if this effect is real, some other reaction must affect the electrode potential. The slopes obtained seem to indicate that oxide formation is not the only cause, but an alternative explanation for this change of slope has not been found.

If a number of reactions are proceeding at the electrode

surface as postulated above, it can be easily seen that drifts of e.m.f. are inevitable. It could be possible to reduce these drifts and transients by depositing a less porous rhodium layer on the 'base' electrode. This could be achieved by employing a lower current density during the rhodium deposition (see sections 6.1.1 and 6.5).

In conclusion, it has been shown that these rhodium electrodes are best deposited on rhodium 'bases' rather than platinum 'bases'. Amine buffers should preferably be avoided (see section 6.1.4 and ref. 80) and the deposition procedure should be modified, as above. However, even if these improvements were carried out, in view of all the interferences, it is unlikely that this electrode could be suitable for precise steady state measurements. On the other hand, as will be seen in the final chapter, an electrode of this kind could be very suitable for automatic titrations.

Chapter 7

DISCUSSION

In Chapter 1, the merits and drawbacks of the various electrodes used for pH measurement were discussed in some detail, and a case was made for the use of metal-metal oxide systems as pH electrodes. In some of the preceding chapters an attempt assessing the viability of a number of metal-metal oxide electrodes was made. This final chapter is intended mainly to provide a brief summary of the properties of the electrodes investigated and to discuss the general viability of metal-metal oxide electrodes.

The pH responses and general properties of the various electrodes were discussed in detail in the relevant chapters and Table 7.1 provides a summary of important points relating to the use of these electrodes for pH measurement. Hydrogen gas and glass electrodes have been included for comparison purposes.

It will be recalled that one of the possible uses for metal-metal oxide electrodes mentioned in Chapter 1 was as reference electrodes which do not require the use of a liquid junction. The results quoted in the previous chapters, however, show that there can be little doubt that electrodes of this kind are quite unsuitable for this purpose. Not only do these electrodes show an appreciable response to pH change, as was suggested in Chapter 1, but also electrode potentials obtained

are prone to drift in most cases. Any plateaux in potential - pH lines obtained during this investigation were found to be associated with drifting potentials and were either due to changes in electrode process or to the presence of interferent species in solution. In addition there is some indication that the nature of the potential - pH line obtained is affected to some extent by the method by which the solution pH is changed; that is whether or not the electrode is removed from solution between measurements. The characteristics referred to above were shown, in Chapter 1, to be undesirable in a reference electrode.

The other, more realistic, possible application for electrodes of this kind is as indicator electrodes. While these electrodes do display a pH response which approximates to the theoretical -59.2 mV per pH, truly reproducible results are only obtained for antimony.

In many cases, changes of slope are observed and these are always accompanied by potential drifts. It was shown in Chapter 6 that several reactions take place when a 'deposited rhodium' electrode is placed in solution, and that these reactions were responsible for the observed potential drifts. It is a reasonable assumption that the potential drifts observed for other electrodes have similar origins. It will be recalled that the electrode potential of an indicator or reference electrode should be controlled by a single reaction. This is obviously not the case for the electrode system examined in Chapter 6 and is extremely unlikely to apply to the other electrodes examined, with the possible exception of the antimony electrode. In view

of these drawbacks, it is unlikely that any of the electrodes examined (apart from the antimony electrode) could be of any use for precise pH measurements or for continuous monitoring of processes where stable electrode potentials are essential. This does not mean, however, that the electrode could not be used for less precise measurements under conditions which would have adverse effects on the more conventional pH electrodes. Also, as will be seen in a later paragraph, this does not preclude the use of deposited electrodes as pH sensors for automatic titrations carried out using apparatus such as the Mettler titrimeter.

The interfering effect of oxygen on metal-metal oxide electrodes has been widely reported in the literature (see previous chapters). As can be seen in Table 7.1, the existence of such an effect has been reported in the literature for every electrode tested except gold. In this work, a detailed investigation of the effect of oxygen was only carried out for deposited rhodium electrodes as reported in section 6.4.

One inherent problem which has played a part in the fall from favour of the antimony electrode is the unfavourable effect of oxidizing and reducing agents on the measured electrode potential. Since the use of noble metals in the monitoring of redox potentials is well known, it was decided to carry out a brief investigation in order to establish the extent to which the electrode potential is affected by the presence of redox couples in solution.

Figure 7.1 shows the results of experiments carried out by a colleague[81] using electrode G2 and a platinum 'spade electrode'.

Electrode G2 and Platinum Spade

in Redox Titration

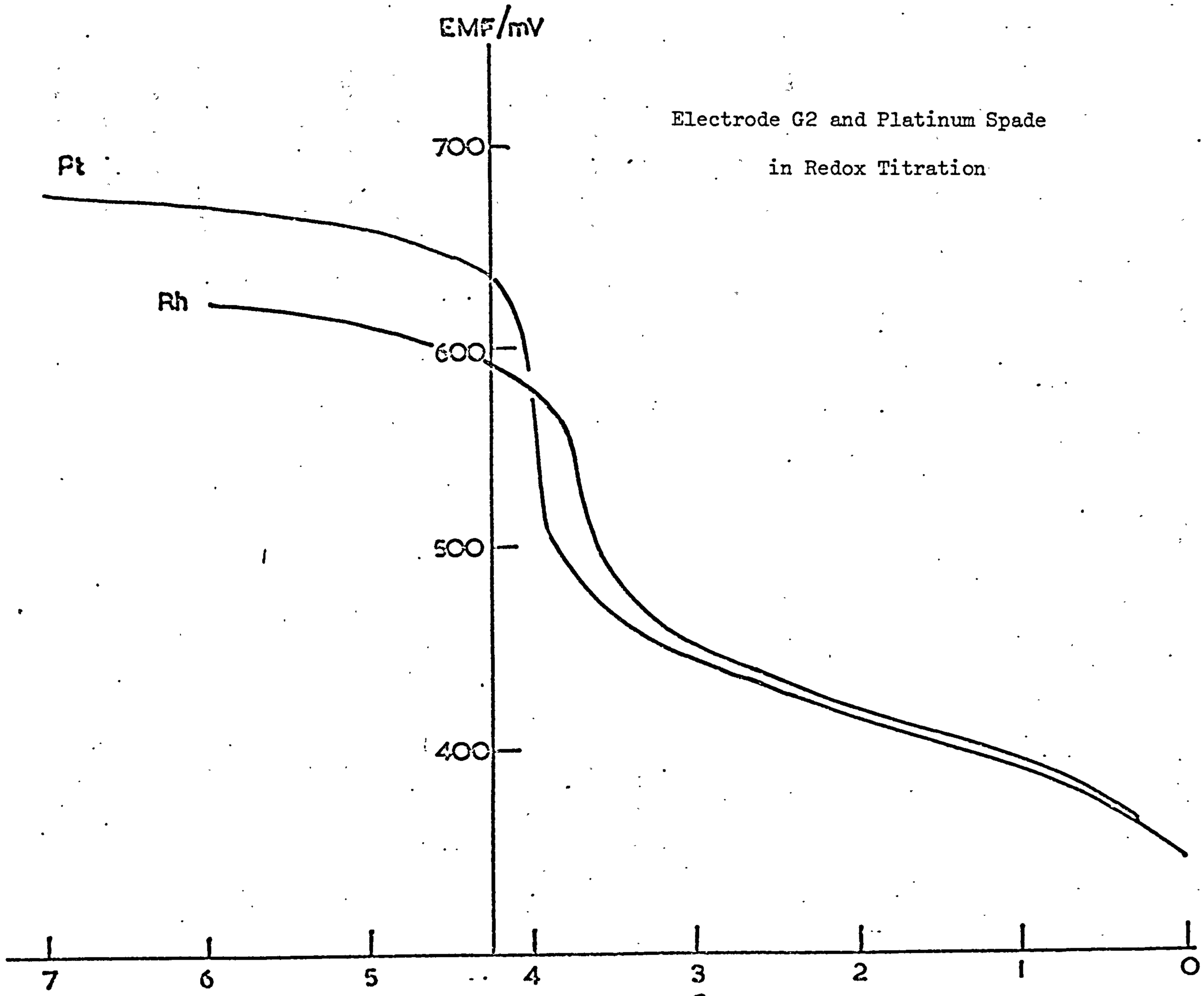


Fig 7·1 Vol.of dichromate/cm^3

The illustrated experiment involved the titration of 25 cm^3 of ferrous ammonium sulphate (0.1 M) by potassium dichromate (0.1 M). It can be clearly seen that although the change of potential for electrode G2 is less than that for a platinum electrode the potential change is still substantial. The response obtained from electrode G4 was identical to that of electrode G2. When an antimony electrode was subjected to the same treatment after an initial increase in electrode potential, in the region of the end point, after 'levelling off', the electrode potential fell to a value approximately 150 mV less positive than the initial potential.

Although the electrode system described in Chapter 6 has been shown to be unsuitable for precise long term measurements preliminary work shows these electrodes to be admirably suitable for automatic titrations. The continuous titrations described previously were relatively slow and so some titrations of 5 cm^3 of sodium hydroxide (0.1 M) with hydrochloric acid (0.1 M) were carried out using electrode G2 or a Radiometer electrode and a Radiometer S.C.E. Figures 7.2 and 7.3 show first differential plots (dE/dV Volume) obtained from two such experiments. The more pronounced and pointed the peak obtained, the more rapid the response of the electrode potential to pH change. In these figures the second peak indicates the end point of the reaction, while the first peak is due to a small, variable amount of carbonate in solution.

It can be clearly seen that, in this case, electrode G2 showed a more rapid response than the glass electrode, although it should be pointed out that the glass electrode employed was

dE/dV against Volume Plot
for Electrode G2

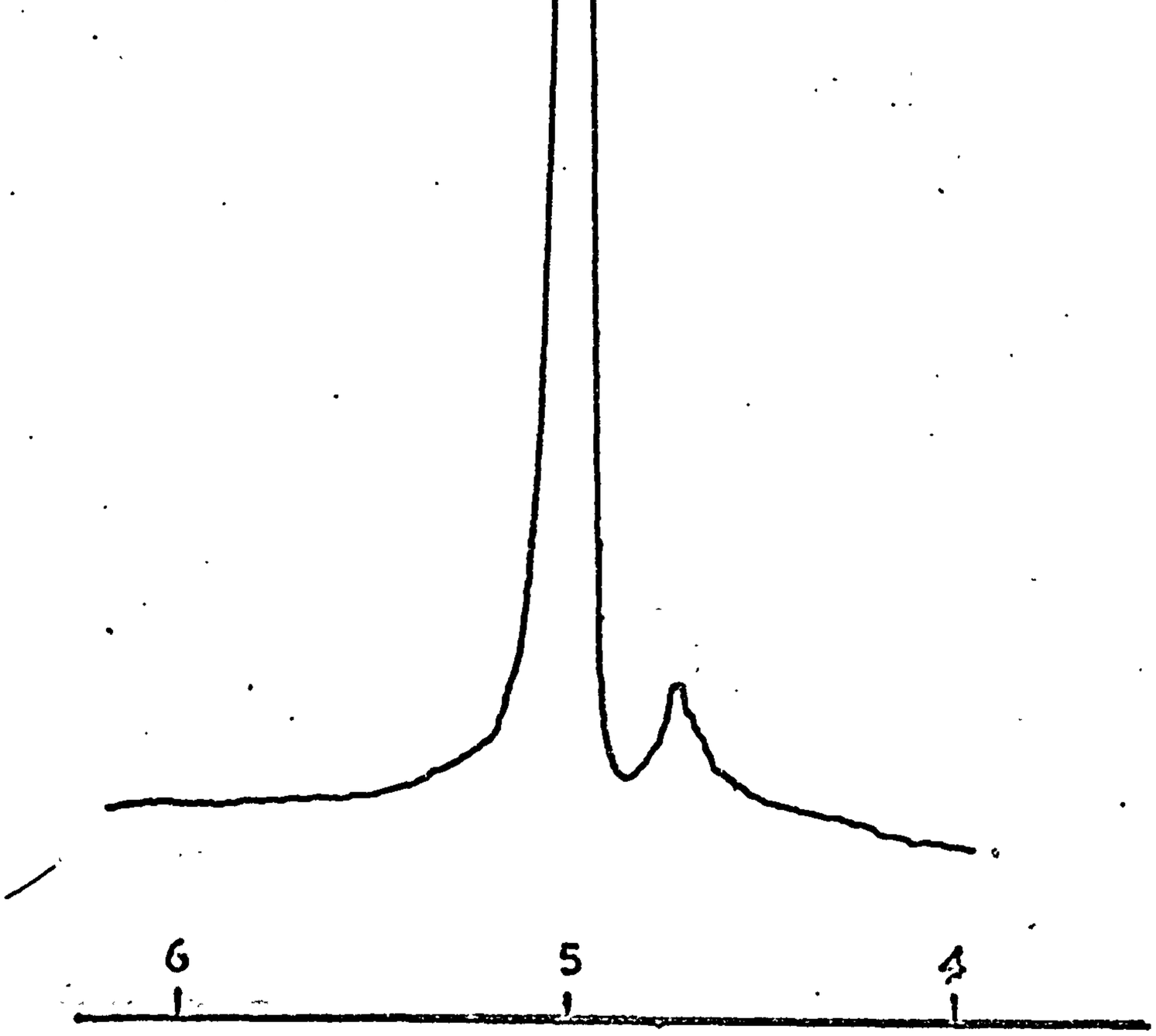


Fig. 7·2 Vol. of 0·01M HCl /cm^3

dE/dV against Volume Plot for

Radiometer Glass Electrode

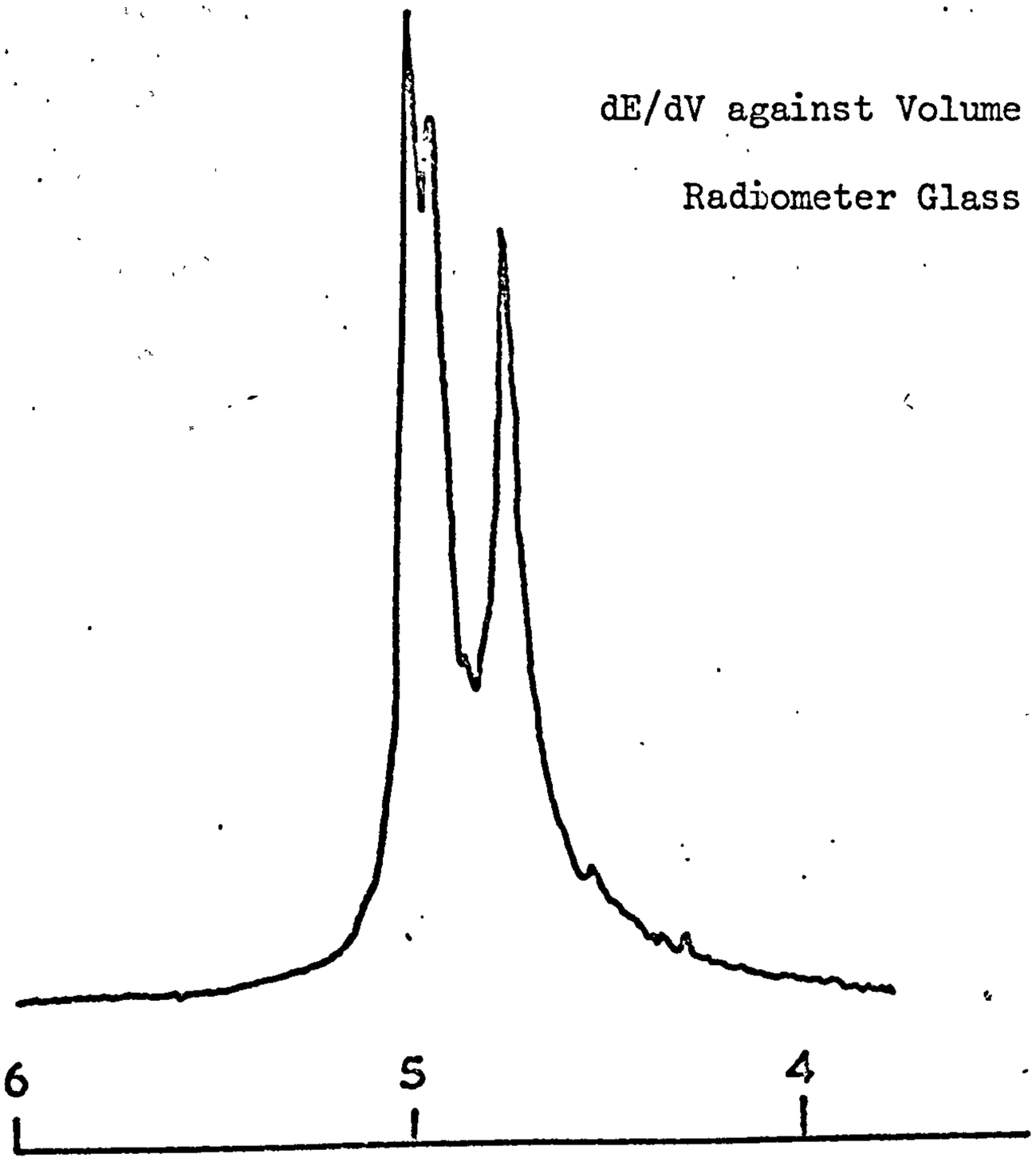


Fig. 7·3. Vol. of 0·01 M HCl / cm^3

not new and glass electrodes with extremely rapid responses are available. Nevertheless it is quite clear that this electrode system could be useful for automatic titrations particularly in solutions damaging to the glass electrode.

Finally, to conclude this work, it will be useful to consider possibilities for further work of a similar nature. The numerous interferences observed indicate that it would be fruitless to investigate noble metal electrodes other than as pH sensors for automatic titrations. Although most metal-metal oxide systems have been investigated in the past, there is still some scope for further investigations although these should be limited to metals with a single oxide species, thus ensuring that interferent reactions are less likely to be observed. Recently, the use of stainless steel as reference electrodes has been reported in the literature[82,83] and work on this subject could be extended to include other alloys. A project on stainless steel electrodes is, at present, under investigation in this laboratory.[81]

Table 7.1

COMPARISON WITH OTHER ELECTRODES

Metal	Oxide	Lit. slope Values	Breaks or Plateaux	This work (slope values)	Oxygen Effect	Interferences
Sb	Sb_2O_3	-50 to -59	pH 2,5,8	-52 to -58	YES	Anions of hydroxy acids Ox. & Red. agents Copper ions, KCl
Bi	BiO_2	-20 to -58	pH 4,8,5 & 11	-58 above pH 7.5	YES	Salt effects. Less sensitive to ox. & red. agents
W	WO_3 WO_2	-57 to -59	-	-31 to -52	YES	Soluble in alkali, Passivated in acids
Pt	PtO_2 $Pt(O)_x$	-60	-	-40 overall (pH 8-4)	YES	No information.
Rh	Rh_2O_3 $Rh(O)_x$	-60	-	-38 to -48	YES	"
Au	Au_2O_3 Au_2O	-60	-	-24 to -59 a	NO	"
Rh (deposited)	Rh-O $Rh(-O)_x$ Rh_2O_3	-	pH 6-7 sigmoid shape see Ch.6	-59 see Ch.6	YES	Ox. & Red. agents Amine buffers
Hydrogen electrode		-59	-	-	-	Oxidizing agents Reducible organic & inorganic cpds, some metal cations Cyanides
Glass electrode		-59	-	-	-	Dehydrating solutions, some colloids, fluorides and surface deposits

a. Depending on method of oxidation

Appendix 1

Throughout this work, the instrument used for the measurement of potential and pH, has been the Mettler titrimeter (Chapter 2). The calibration described below is based on a draft British Standard relating to the calibration of laboratory pH meters (BS 3145).[84]

The Mettler titrimeter, comprising modules DK10, DK11 and DK12, has a deflection type scale for mV measurements, but the large scale intervals (20 mV and 100 mV) do not permit sufficiently precise measurements to be taken. A greater degree of precision is, however, available using the built-in null meter (0 to $\pm$ 50 mV, Δ 0.5 pH) in conjunction with a thumbwheel-type potentiometer. A selector switch enables pH, and both negative and positive potentials to be measured using this arrangement. Potentials of 0 to 1,999 mV are measurable in intervals of 1 mV, while pH values from 0 to '19.99' can be measured in intervals of 0.01 pH. The addition of a Fenlow digital voltmeter permitted measurements to be made to 0.1 mV or 0.001 pH , although in practice, this facility was only used to obtain values to the nearest 0.01 pH unit or 1 mV.

'Slope' adjustment from 0 to $\pm$ 69.9 is effected on this instrument by means of another thumbwheel while two calibration adjustments are available, marked E_{is} and pX_{is}. Under normal circumstances, however, the instrument is calibrated using the 'pX_{is}' thumbwheel (0 to $\pm$ 9.99) only. The E_{is} is normally set at 0 unless data from several isotherms are available. A manual

temperature compensating device (slope factor compensation) is fitted and this permits the temperature setting to be varied from 0 to 100°C (5° intervals).

It is specified in draft BS 3145 [84] that, "the calibration of the pH meter scale is carried out using a potentiometer having a scale interval in mV equal to one fifth of the numerical value of the scale interval of the pH scale" and "the principal mV scale is tested at 100 mV intervals using a potentiometer which has a scale interval at least one fifth of that of the scale being tested." The calibrations reported in this appendix refer to measurements made with a potentiometer having a scale interval in mV equal to one tenth of the mV scale. The figures reported for measurements made using the D.V.M. are quoted to the nearest 0.1 mV and 0.001 pH for completeness, but in order to comply with BS 3145, these figures should be taken to the nearest mV as 0.01 pH only.

Before examining the titrimeter, it was decided to calibrate the D.V.M. in order to ensure that any deviations detected were due to the titrimeter alone. These figures are given in Table A1. The calibrations of the entire instrument in terms of potential is shown in Table A2.

The draft British Standard specifies that, before checking the pH scale, the temperature compensator must be set to 25°C and the isopotential control must be set to 7. This was done using the pX_{is} control. The E_{is} control, however, was left at zero since it was found that this yielded a null meter / thumbwheel indication of 7 when the terminals of the meter were shorted. (For potential measurements, the meter was set to zero

with the terminals shorted.) It was found that when the meter was set up in this way, no discernible change was observed when the temperature control was varied between its extreme settings (see ref. 84). Finally, the meter was calibrated by applying potentials corresponding to increments of 1 pH. These applied potentials were calculated using a slope factor constant (k) of-59.159 mV/pH at 25°C (see Chapter 1). The calibration of the pH scale is given in Table A3. In all the tests described above, measurements are made with both increasing and decreasing incremental applied potential differences to test for hysteresis.

The isopotential and manual temperature compensation devices were checked using the following procedures recommended in BS 3145.[84]

With the input terminals shorted and the temperature compensation set to 25°C, the null meter/thumbwheel was set to 7.00 (the same value as set on the pX_{is} thumbwheel). The manual temperature compensator was changed from 0°C to 50°C and the change in the indicated value noted. In the case of the null meter, there was no discernible deviation and in the case of the D.V.M., the observed difference was 0.005 pH.

Having reset the indicated null meter/thumbwheel value so that no change was observable when the above test was applied (not necessary in this case), the potentials given in Table A4 were applied across the input terminals and corresponding temperature values were set on the manual temperature compensator. The indicated pH change should equal 7 pH. The observed 'deflections' are also given in Table A4.

In draft BS 3145,[84] two tests to investigate the input current characteristics of the instrument are recommended. The first test involves shorting the terminals and adjusting the apparatus until the indicator reads pH 7.00 then a screened 10 GΩ (± 10%) resistor is connected across the inputs and the change in reading observed. In this case, the change amounted to -0.001 pH for the digital output and 0.00 pH for the null meter/thumbwheel.

This test gives an indication of the input current at zero voltage. In the second test, designed to measure the input current change per volt, 0.5 V is applied across the inputs and the instrument is adjusted so that the meter reads a value on scale. A 10 GΩ screened resistor is then put in series with the voltage source and the change in reading observed. The polarity of input voltage is then reversed and the observation repeated. The difference between the greater of these two changes in reading and that given in the previous test is noted. The greater change in reading was +0.002 pH for the digital output and 0.00 pH for the null meter/thumbwheel.

The information obtained from this investigation is summarized in Table A5, along with the permitted errors for each test.

Table A1 Calibration of D.V.M.

D.V.M. negative mV		Potentiometer mV	D.V.M. positive mV	
0.0	0.0	0	0.0	0.0
100.0	100.0	100.0	100.0	100.0
200.0	200.0	200.0	200.0	200.0
300.0	300.0	300.0	300.0	300.0
400.0	400.0	400.0	400.0	400.0
500.0	500.0	500.0	500.0	500.0
600.0	600.0	600.0	600.0	600.0
700.0	700.0	700.0	700.0	700.0
800.0	800.1	800.0	800.0	800.0
900.0	900.1	900.0	900.0	900.0
1000.1	1000.1	1000.0	1000.0	1000.0
1100.1	1100.1	1100.0	1100.0	1100.0
1200.1	1200.1	1200.0	1200.0	1200.0
1300.1	1300.1	1300.0	1300.0	1300.0
1400.1	1400.1	1400.0	1400.0	1400.0
1500.1		1500.0	1500.0	

Table A2

D.V.M. -ve mV	Null -ve mV	D.V.M. -ve mV	Null -ve mV	Potentio-meter mV	D.V.M. +ve mV	Null +ve mV	D.V.M. +ve mV	Null +ve mV
1.0	1	1.0	1	0.0	- 0.9	- 2	- 0.9	- 2
100.8	101	100.9	101	100.0	98.8	98	98.8	98
200.8	201	200.8	201	200.0	198.7	198	198.7	198
300.6	301	300.7	301	300.0	298.6	298	298.6	298
400.6	401	400.6	401	400.0	398.5	397	398.5	398
500.5	501	500.5	501	500.0	498.4	497	498.4	497
600.4	601	600.4	601	600.0	598.3	597	598.3	597
700.3	701	700.3	701	700.0	698.2	697	698.2	697
800.2	800	800.2	800	800.0	798.1	797	798.1	797
900.1	900	900.1	900	900.0	898.1	897	898.1	897
1000.0	1001	1000.0	1001	1000.0	998.0	997	998.0	997
1099.9	1101	1099.9	1101	1100.0	1099.9	1097	1097.9	1098
1199.8	1201	1199.8	1201	1200.0	1197.8	1198	1197.8	1198
1299.7	1301	1299.7	1301	1300.0	1297.7	1297	1297.7	1297
1399.6	1401	1399.6	1401	1400.0	1397.7	1397	1397.6	1397
1499.5	1501			1500.0	1497.6	1497		

Table A3 (Slope adjustment set to-59.2 mV/pH)

D.V.M. (pH)	Null (pH)	D.V.M. (pH)	Null (pH)	Applied Potentials (mV)	Corresponding pH change	D.V.M. (pH)	Null (pH)	D.V.M. (pH)	Null (pH)
7.006	7.00	7.006	7.00	0.0	0.00	7.007	7.01	7.007	7.01
6.009	6.01	6.009	6.01	59.2	1.00	8.004	8.00	8.003	8.00
5.012	5.01	5.012	5.01	118.3	2.00	9.001	8.99	9.001	9.00
4.015	4.01	4.014	4.01	177.5	3.00	9.997	9.99	9.997	9.99
3.018	3.02	3.017	3.01	236.6	4.00	10.994	10.99	10.994	10.99
2.021	2.02	2.020	2.01	295.8	5.00	11.991	11.99	11.990	11.99
1.022	1.02	1.021	1.02	335.0	6.00	12.990	12.99	12.988	12.99
0.024	0.02			414.1	7.00	13.986	13.99	13.985	13.99
				473.3	8.00	14.983	14.98		

Table A4 (Slope adjustment set to-59.2 mV/pH)

Temp. (°C)	Applied Potential (mV)	D.V.M. (pH)	Null (pH)
25	0.0	7.007	7.01
0	379.4	0.022	0.02
40	434.9	0.027	0.03
60	462.7	0.015	0.01
80	490.5	0.034	0.03
100	518.3	0.060	0.06
80	490.5	0.034	0.03
60	462.7	0.016	0.01
40	434.9	0.030	0.03
0	379.4	0.022	0.02

Table A5

Test	Permitted Error S.i. r.u.*	Null		Pass/ Fail	D.V.M.	Pass/ Fail
Scale interval/ representation unit		Null Thumbwheel	0.1 pH 0.01 pH		0.01 pH	
Indication	20%	1	0.02 pH	P	0.02 pH	F
Isopotential	20%	1	0.00 pH	P	0.005 pH	P
Manual temperature compensation	2	10	0.06 pH	P		
Scale marking on Temp. Comp. Device	2^{o}		5^{o}	F		
Input current at zero voltage	10	50	0.00 pH	P	-0.001 pH	P
Difference between two input current tests	2	10	0.00 pH	P	+0.003 pH	P

* S.i. - scale interval
r.u. - representation unit

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